(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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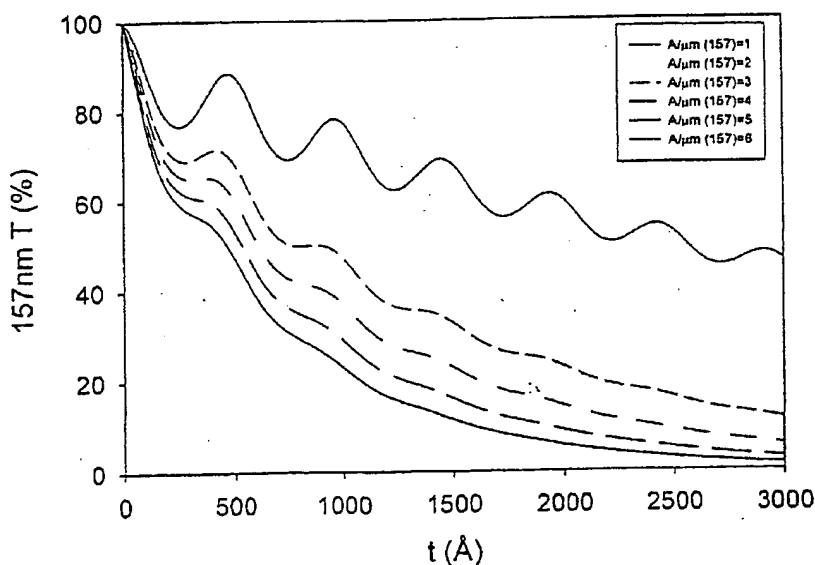**(75) Inventors/Applicants** *(for US only):* **WHELAND, Robert, Clayton** [US/US]; 510 Twaddell Mill Road, Wilmington, DE 19807 (US). **FRENCH, Roger, Harquail** [US/US]; 1516 Athens Road, Wilmington, DE 19803 (US). **SCHADT, Frank, Leonard III** [US/US]; 2407 Delaware Avenue, Wilmington, DE 19806 (US). **ZUMSTEG, Frederick, C., Jr.** [US/US]; 2715 Silverside Road, Wilmington, DE 19810 (US).

(54) Title: COPOLYMERS FOR PHOTORESISTS AND PROCESSES THEREFOR

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(57) Abstract: Fluoroolefin/acid group or protected acid group-containing copolymers for photoresist compositions and microlithography methods employing the photoresist compositions are described. These copolymer compositions comprise 1) at least one fluoroolefin, preferably hexafluoroisobutylene, and 2) an acid group or a protected acid group (e.g., a t-alkyl ester, preferably a t-butyl ester), which together impart high ultraviolet (UV) transparency and developability in basic media to these materials. The materials of this invention have high UV transparency, particularly at short wavelengths, e.g., 157 nm and 193 nm, which makes them useful for lithography at these short wavelengths.

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TITLE
COPOLYMERS FOR PHOTORESISTS AND PROCESSES THEREFOR
BACKGROUND OF THE INVENTION

Cross-Reference to Related Applications

This application claims the benefit of prior filed copending provisional application 60/201,143 filed on May 5, 2000 which is incorporated herein by reference in its entirety.

1. Field of the Invention

The present invention pertains to a copolymer containing a first repeat unit derived from a fluoroolefin and a second repeat unit derived from an ethylenically unsaturated monomer containing an acid group or a protected acid group which cocopolymer is useful in a photoresist composition for imaging in the production of semiconductor devices.

2. Background

In the process for manufacturing semiconductor devices, very fine features are etched onto a substrate, typically a silicon wafer. The features are formed on the substrate by electromagnetic radiation which is impinged, imagewise, on a photoresist composition applied to the silicon wafer. Areas of the photoresist composition which are exposed to the electromagnetic radiation change chemically and/or physically to form a latent image which can be processed into an image for semiconductor device fabrication. Positive working photoresist compositions generally are utilized for semiconductor device manufacture.

The photoresist composition typically is applied to the silicon wafer by spin coating. The silicon wafer may have various different material layers applied to it in other processing steps. In addition, in a particular photolithographic processing step, the silicon wafer may have a hard mask layer, typically of silicon dioxide or silicon nitride, applied below the photoresist composition layer. In addition, an antireflective layer (ARC) may be applied below the photoresist composition layer, by a coating process (and is then typically referred to as a bottom anti-reflective (BARC)) or on top of the photoresist composition layer (and typically called a top-anti reflective layer (TARC)). Typically the thickness of the resist layer is sufficient to resist the dry chemical etch processes used in transferring a pattern to the silicon wafer.

Various copolymer products for photoresist compositions have been described in Introduction to Microlithography, Second Edition by L. F. Thompson, C. G. Willson, and M. J. Bowden, American Chemical Society, Washington, DC, 1994.

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The photoresist composition generally comprises a film forming copolymer which may be photoactive and a photosensitive composition that contains one or more photoactive components. As described in the Thompson et al. publication, upon exposure to electromagnetic radiation (e.g., UV light), the

5   photoactive component acts to change the rheological state, solubility, surface characteristics, refractive index, color, electromagnetic characteristics or other such physical or chemical characteristics of the photoresist composition.

The use of ultraviolet light of lower wavelength corresponds to higher resolution (lower resolution limit). Lithography in the UV at 365 nm (I-line) is a

10   currently established image-forming process for making semiconductor devices. The features formed by this process have a resolution limit of about 0.35-0.30 micron. Known photoresist compositions for lithography using a 365 nm wavelength are made from novolak copolymers and diazonaphthoquinones as dissolution inhibitors. Lithography in the deep UV at

15   248 nm has been found to have a resolution limit of approximately 0.35-0.13 micron. The known photoresist compositions for this process are made from p-hydroxystyrene copolymers. Lithographic processes using electromagnetic radiation at even shorter wavelengths are looked to for forming very fine features because the use of lower wavelengths correspond to higher

20   resolution; that is, in deep (wavelength less than 300 nm), vacuum (wavelength less than 200 nm) or even the extreme (wavelength less than 30 nm) ultraviolet. However, at wavelengths of 193 nm or shorter, the photoresist compositions known for use at 365 nm and 248 nm have been found to lack sufficient transparency.

25   A key difficulty encountered in developing copolymers for use in photoresist compositions that are imaged at lower wavelengths, e.g., 157 nm, is the lack of transparency at these low wavelengths. The transparency requirements for photoresist compositions are usually on the order of allowing about 20 to about 40% of incident light to penetrate the full thickness of the resist layer to

30   produce an image with well-defined, vertical side walls, which are important in achieving high resolution and minimizing defects. Copolymers which lack transparency absorb too much light and thereby produce an unacceptable image with low resolution and too many defects.

A thick film layer of the photoresist material is beneficial for high

35   resolution and low defects. However, thick films tend to lack transparency at low wavelengths. To determine the absorbance requirements of a copolymeric material that will allow about 20 to about 40% of incident light to penetrate the resist film layer, the light transmission (T) for a thin copolymeric resist film layer,

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considering the effects of optical interference in the film, was calculated as a function of the film thickness in angstroms (t) and the optical absorbance per micron (of film thickness) of a film layer containing the copolymer. The results are shown for a copolymeric resist for use at 157 nm in Figure 1 and for a

5   copolymeric resist for use at 193 nm in Figure 2. In this calculation an index of refraction (n) for the resist of 1.6 is used and no effect(s) of the underlying silicon substrate, representing the light transmitted through an unsupported copolymer film layer have been considered to represent the light transmitted through an unsupported film. As shown in Figure 1, that for films of approximately

10   1300 angstroms thickness to achieve a transmitted light intensity at 157 nm of about 20% can require a copolymer film with an absorbance per micron (of film thickness) at 157 nm below 5 per micron ($< 5 \ \mu m^{-1}$). For use at 193 nm, as shown in Figure 2, that for films of approximately 5500 angstroms thickness, to achieve a transmitted light intensity at 193 nm of about 25% can require a copolymer film

15   with an absorbance per micron (of film thickness) at 193 nm below 1 per micron (less than 1 μm^{-1}), while for a film thickness of 4000 angstroms, a copolymer film having an absorbance per micron of 2 per micron (2 μm^{-1}) can have a transmitted light intensity at 193 nm of only about 14%. Accordingly, the thicker a film gets, the lower absorption it must have to transmit a reasonable percentage of incident

20   short wavelenght light.

      The molecular weight of a polymer for a photoresist composition which is sufficient for high film-forming properties may be detrimental to transparency at low wavelengths. Table 1 below shows the known absorption maxima for simple hydrocarbon $H(CH_2)_nH$ and fluorocarbon $F(CF_2)_nF$ chains. As these chains

25   become longer, their absorption moves to longer wavelengths, first starting up at 157 nm for hydrocarbons when n is greater than 1 and for fluorocarbons when n is greater than about 10. This implies that polymers having $(CH_2)_n$ chain segments with n greater than 1 and $(CF_2)_n$ segments with n greater than about 10 are likely to be highly absorbing at 157 nm. One of the problems faced therefore by one

30   wanting to make resists highly transparent to 157 nm light is how to achieve polymeric molecular weights, especially molecular weights sufficient for film-forming capability, while avoiding long $(CH_2)_n$ and $(CF_2)_n$ chains which hinder tranparency.

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Table 1. Comparison of UV Absorption Maxima for Hydrocarbons and Fluorocarbons		
$X(CX_2)_nX$	WAVELENGTH OF ABSORPTION MAXIMUM	
	$X = H^1$	$X = F$
n = 1	143 nm & 128 nm	
n = 2	158 nm & 132 nm	
n = 3	159 nm & 140 nm	119 nm[1]
n = 4	160 nm & 141 nm	126 nm[1]
n = 5	161 nm & 142 nm	135 nm[1]
n = 6	162 nm & 143 nm	142 nm[1]
n = 7	163 nm & 143 nm	
n = 8	163 nm & 142 nm	
N = 172		161 nm[2]

1. B. A. Lombos, P. Sauvageau, and C. Sandorfy, *Chem. Phys. Lett.*, 1967, 42.
2. 2. K. Seki, H. Tanaka, T. Ohta, Y. Aoki, A, Imamura, H. Fujimoto, H. Yamamoto, H. Inokuchi, *Phys. Scripta*, 41, 167(1990).

5   Even when a copolymer film for use in imaging at 157 nm is only 1500 Å thick, very few organic copolymers have been found that allow about 20 to about 40% of 157 nm light to penetrate or, that is, that have an (optical) absorbance per micron (absorbance (A) per micron of film thickness t) of less than 3 μm^{-1}. For example, of 12 candidate copolymer systems tested, Bloomstein et. al. (*J. Vacuum*

10   *Sci. Technol.*, B16, 3154 (1998)) report only three copolymers having an absorbance per micron less than 3 μm^{-1}. These three copolymers are Teflon™ AF having an absorbance per micron of about 0.5 μm^{-1}, poly(methysiloxane) having an absorbance per micron of about 1.5 μm^{-1}, and poly(phenylsiloxane) having an absorbance per micron of about 2.5 μm^{-1}. Attempts to convert these pure

15   copolymers into thin films both sensitive to light and capable of aqueous base development have tended to increase absorption at 157 nm. Indeed, none of the three transparent copolymer systems found by Bloomstein have yet been successfully converted into practical resists. There is a need for photosensitive, aqueous base developable copolymers sufficiently transparent to UV light to make

20   a good resist. Resists effective at 157 nm should also work at longer wavelengths (for example, 193 and 248 nm).

       Because photolithography at the shorter wavelengths would provide the very fine features having lower resolution limits; that is, a resolution limit of approximately 0.18-0.12 micron at 193 nm, approximately 0.07 micron at 157 nm

25   photoresist compositions that will be sufficiently transparent at these short wavelenths are needed.

       There is a need for suitable photoresist compositions for use at 193 nm and lower, particularly at 157 nm, that have not only high transparency at these short

wavelengths but also other key properties, including good plasma etch resistance, development characteristics, and adhesive properties.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a plot of the % transmission (T) at 157 nm of resist films with
5   optical absorbance per micron at 157 nm in units of inverse microns of $1/\mu m$ to $6/\mu m$ versus the resist film thickness (t) in angstroms. Transmission was calculated for air underlying the resist film so as to neglect the underlying semiconductor wafer.

Figure 2 is a plot of the % transmission (T) at 193 nm of resist films with
10   optical absorbance per micron at 193 nm in units of inverse microns of $1/\mu m$ to $2/\mu m$ versus the resist film thickness (t) in angstroms. Transmission was calculated for air underlying the resist film so as to neglect the underlying semiconductor wafer.

Figure 3 is a plot of the optical absorbance per micron in units of inverse
15   microns for P(HFIB/VF/tBA) (copolymer of Example 1) versus wavelength lambda (λ) in units of nanometers.

Figure 4 is a plot of the optical absorbance per micron in units of inverse microns for P(HFIB/VF/tBA) (copolymer of Example 2) versus wavelength lambda (λ) in units of nanometers.

20   Figure 5 is a plot of the optical absorbance per micron in units of inverse microns for P(HFIB/VF2/tBA) (copolymer of Example 3) versus wavelength lambda (λ) in units of nanometers.

Figure 6 describes the optical absorbance per micron in units of inverse microns for P(HFIB/VF2/tBA) (copolymer of Example 4) versus wavelength
25   lambda (λ) in units of nanometers.

Figure 7 is a plot of the optical absorbance per micron in units of inverse microns for P(HFIB/VAc/tBA) (copolymer of Example 5) versus wavelength lambda (λ) in units of nanometers.

Figure 8 is a plot of the optical absorbance per micron in units of inverse
30   microns for P(HFIB/VF2/tBA) (copolymer of Example 7) versus wavelength lambda (λ) in units of nanometers.

Figure 9 is a plot of the optical absorbance per micron in units of inverse microns for P(HFIB/VF2/tBMA) (copolymer of Example 8) and a formulated photoresist (8B of Example 8) of P(HFIB:VF2:tBMA) versus wavelength lambda
35   (λ) in units of nanometers.

Figure 10 is a plot of the optical absorbance per micron in units of inverse microns for P(HFIB/VF2/tBMA) (copolymer of Example 9) and two formulated

photoresists (9A and 9B of Example 9) of P(HFIB:VF2:tBMA) versus wavelength lambda (λ) in units of nanometers.

Figure 11 is a plot of the optical absorbance per micron in units of inverse microns for P(HFIB/tBA) (copolymer of Example 10) and a formulated

5   photoresist (10B of Example 10) of P(HFIB/tBMA) versus wavelength lambda (λ) in units of nanometers.

SUMMARY OF THE INVENTION

In one embodiment, the invention is a copolymer comprising:

(a)   a first repeat unit derived from at least one fluoroolefin having the

10   structure:

$$(H)(H)C=C(R_1)(R_2)$$
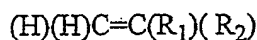
wherein R_1 and R_2 are independently selected from the group consisting of

15   C_1-C_3 perfluoroalkyl, or taken together are $(CF_2)_n$ wherein n is 3 to 5; and

(b)   a second repeat unit derived from a first ethylenically unsaturated comonomer comprising an acid group or a protected acid group.

In another embodiment, the invention is directed to a photoresist comprising the copolymer and at least one photoactive component.

20   In yet another embodiment, the invention is directed to a process for preparing a photoresist image on a substrate comprising

(A)   applying the photoresist composition of this invention to a substrate to form a photoresist layer,

(B)   imagewise exposing the photoresist layer to form imaged and non-

25   imaged areas; and

(C)   developing the exposed photoresist layer having imaged and non-imaged areas to form the photoresist image on the substrate.

With respect to some specific embodiments of the photoresists, the copolymer comprising a first repeat unit derived from a fluoroolefin and a second

30   repeat unit derived from (meth)acrylate ester-containing copolymer present as a component in a photoresist preferably has an optical absorbance per micron of less than 5.0 μm^{-1} at a wavelength of 157 nm. In other certain embodiments, the copolymer comprising a first repeat unit derived from a fluoroolefin and a second repeat unit derived from (meth)acrylate ester-containing copolymer can be further

35   comprised of an aliphatic polycyclic functionality. In some embodiment(s), the photoactive component can be a photoacid generator. In still other embodiment(s), the photoresists can be further comprised of a dissolution inhibitor.

DETAILED DESCRIPTION OF THE INVENTION

A key characteristic of the copolymers (and photoresists comprised of the copolymers) of this invention is the cooperative combination in the copolymer of the first repeat unit with the second repeat unit. Another characteristic of the

5   copolymer is that it does not detrimentally absorb in the vacuum and far UV. The minimization of functionality, such as aromatic groups, which absorb in the ultraviolet in the repeat units of the copolymer is desirable in order for the copolymer to possess suitable, preferably high, optical transparency.

The first repeat unit is derived from a fluoroolefin having the structure:
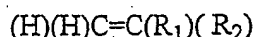
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$$(H)(H)C=C(R_1)(R_2)$$

wherein R_1 and R_2 are independently selected from the group consisting of C_1-C_3 perfluoroalkyl, or taken together are $(CF_2)_n$ wherein n is 3 to 5. Suitable

15   examples of specific comonomers include, but are not limited to, hexafluoroisobutylene and decafluoroisohexylene.

The second repeat unit is derived from a first ethylenically unsaturated comonomer comprising an acid group or a protected acid group. Suitable, but non-limiting examples of an acid group or a protected acid group for this

20   invention are described below in the section entitled "Protective Groups for Removal by PAC Catalysis".

There can be a third, optional, repeat unit derived from a second ethylenically unsaturated comonomer. In one embodiment, the second ethylenically unsaturated comonomer has the structure CXY=CWZ where X and

25   Y and W can be a fluorine atom or a hydrogen atom and Z can be a fluorine atom, a hydrogen atom, a chlorine atom (when X, Y and W are fluorine), -OH (when W is H), or -O(C=O)R where $R = C_pA_{2p+1}$ in which A is any combination of hydrogen and fluorine atoms +- which the number of fluorine atoms exceeds the number of hydrogen atoms and p is an integer ranging from 1 to 3.

30   Suitable, non-limiting examples of second ethylenically unsaturated comonomers are vinyl fluoride, vinylidene fluoride, vinyl acetate, trifluoroethylene, chlorotrifluoroethylene, tetrafluoroethylene, 4,5-difluoro-2,2-bis(trifluoromethyl)-1,3-dioxole (perfluorodimethyldioxole), 2,2-bis(trifluoromethyl)-1,3-dioxole (dihydroperfluoromethyldioxole), vinyl alcohol

35   (i.e., a vinyl acetate unit hydrolyzed after copolymerization), 1,3-dioxole-2-one (vinylene carbonate), and maleic anhydride.

The copolymers of this invention preferably are characterized by a repeat unit derived from at least one first ethylenically unsaturated comonomer

containing an acid group or a protected acid group (e.g., a t-alkyl ester group) that
is present in these copolymers from about 25 to about 60 mole percent and a
repeat unit derived from at least one or more fluoroolefin(s) that are present in the
copolymer from about 40 to about 65 mole percent. The fluoroolefin/t-alkyl ester

5   copolymers more preferably with respect to achieving low optical absorbance per
micron are characterized by a repeat unit derived from at least one first
ethylenically unsaturated comonomer containing protected t-alkyl ester group that
is present in the copolymers at less than or equal to 60 mole percent, and, still
more preferably, at less than or equal to 50 mole percent.

10   As previously noted, it is believed that long hydrocarbon and fluorocarbon
chains in a polymer will be likely to absorb light at 157 nm, making it difficult to
achieve transparent materials with polymeric molecular weights. Thus, it is
believed that alternating short $(CH_2)_n$ and $(CF_2)_m$ segments in the polymer will
be likely to provide a relatively transparent polymer. For example, it has been

15   found that monomers such as vinylidene fluoride in which CF_2 alternates with
CH_2 and hexafluoroisobutylene in which $C(CF_3)_2$ alternates with CH_2 favor
transparency at 157 nm. Although the value of n and m, and the ratio of
hydrocarbon to fluorocarbon in the polymer chain can be varied depending upon
the other components of the photoresist and the other repeat units of the polymer,

20   as one skilled in the art would be able to determine, in general more than two
immediately adjacent CH2 groups (i.e. $(CH_2)_n$ where n is greater than about 2)
and more than about 7 to 10 immediately adjacent CF2 groups (i.e. $(CF_2)_m$ where
m is greater than about 7, more typically greater than about 10) will be likely to
absorb light at 157 nm. The appropriate alternating sequence can be in the

25   monomer from which the polymer is derived. Alternatively, the alternating
sequence can be achieved during the polymerization process by techniques known
in the art.

It is recognized though that there usually will be a minimal level of
protected acid and/or free acid groups present for the copolymer to be soluble

30   and/or dispersible in aqueous basic solutions (e.g., standard 0.262 N TMAH
solution) for developability. This minimal level can vary with the structure of the
moiety bearing the protected acid group and with the selection of comonomer(s)
and their levels in the copolymers as well as with other parameters of the
copolymer such as molecular weight. One skilled in the art can determine readily

35   whether a given copolymer is soluble/dispersible or not in aqueous basic
solutions. This requirement for a suitable minimal level of protected acid groups
and/or free acid groups in the copolymer to impart base solubility/dispersibility to
the copolymer is usually balanced against keeping the level as low as feasible in

order to maximize transparency of the copolymer in the far or vacuum UV range
of the electromagnetic spectrum.

The copolymers of this invention optionally may be further comprised of a
repeat unit derived from a compound comprising an aliphatic polycyclic group.

5   Aliphatic polycyclic groups are of interest because they can often beneficially
increase plasma etch resistance or raise T_g by stiffening a polymer chain. They
can be incorporated in the polymer as part of the chain (as in the case of
norbornene copolymers) or as pendant side groups (as in the case of adamantyl
acrylate copolymers). A suitable aliphatic polycyclic group can contain from

10 about seven to about eighteen carbon atoms, can contain olefinic unsaturation, and
one or more of the ring carbons can be replaced by heteratoms such as oxygen,
nitrogen, and sulfur. Typically, the aliphatic polycyclic group is a fused
polycyclic hydrocarbon containing from about seven to about twelve carbon
atoms with two to four rings. The aliphatic polycyclic group can be substituted or

15 unsubstituted. If the aliphatic polycyclic group is substituted, the substituent
group can contain from one to about four carbon atoms and, optionally,
heteroatoms such as oxygen, nitrogen, sulfur, or halogen such as chlorine or
fluorine. Particularly desirable functional groups are those such as -OH or -
$C(CF_3)_2OCH_2OCH_3$ which aid in wetting, aqueous solubility, and/or

20 photodevelopment while adding relatively little to light absorption.

When the polymers comprise one or more aliphatic polycyclic groups, the
percentage of repeat units of the copolymer containing the aliphatic polycyclic
group ranges from about 5 to about 60 mole percent; and preferably from about 10
to about 50 mole percent.

25 The fluoroolefin copolymers of this invention can contain additional
functional groups beyond those specifically mentioned herein with the proviso
that, preferably, the copolymer is substantially free of aromatic groups and still
more preferably aromatic groups are absent in these copolymers. The presence of
aromatic groups in these copolymers has been found to detract from their

30 transparency and result in their being too strongly absorbing in the near, deep and
vacuum UV regions of the electromagnetic spectrum to be suitable for use in
photoresists that are imaged at wavelengths in the UV. For this reason, in one
embodiment of the invention, the copolymer is free of aromatic groups.

In many embodiments according to this invention, the copolymer has an

35 optical absorbance per micron of less than 5.0 μm^{-1} at a wavelength of 157 nm,
preferably less than 4.0 μm^{-1} at this wavelength, more preferably, less than
3.5 μm^{-1} at this wavelength, and, most preferably, less than 3.0 μm^{-1} at this
wavelength.

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Copolymerization Methods

Copolymerizations can be carried out by any of the common methods known to those skilled in the art including solution, dispersion, or emulsion copolymerizations employing either batch or continuous processes with either an

5   initial single charge, intermittant, or a continuous feed of reactants.

Considering the present small scale of the copolymerizations exemplified herein, the copolymerizations were most conveniently run using a single initial charge of monomers, organic solvent, and initiator to an autoclave.

The contents of the autoclave were then typically agitated under pressure

10   usually about 10 to about 500 psi (about 0.70 to about 35.15 kg/cm^2), typically about 20 to about 100 psi (about 1.41 to about 7.03 kg/cm^2) for about 1 to about 48 hours, typically about 6 to about 18 hours at about 10 to about 100°C, typically about 20 to about 75°C, the temperature and reaction time being chosen to match the half-life of the initiator and the thermal stability of the protected acid groups in

15   the copolymer. Common free radical intiators can be used and include diacyl peroxides such as DP ($CF_3CF_2CF_2OCF(CF_3)(C=O)OO(C=O)CF(CF_3)OCF_2CF_2CF_3$, HFPO dimer peroxide), percarbonates such as Perkadox(TM) 16N [di(4-t-butylcyclohexyl)peroxydicarbonate), and AIBN (2,2'-azobisisobutyronitrile). For

20   example, when DP (HFPO dimer peroxide) is the initiator and t-butyl acrylate is the source of protected acid groups, copolymerizations were frequently run at ambient temperatures (about 20 to about 30°C) for about 8 to about 16 hours.

Organic fluids that do not significantly interfere with radical copolymerization such as fluorocarbons, chlorofluorocarbons,

25   chlorofluorohydrocarbons, and hydrofluorocarbons are desirable solvents for the copolymerization. By interfere with copolymerization we mean solvents that change molecular weight by chain transfer or that terminate copolymerization by reaction with the growing radical ends. Preferred solvents include Vertrel(TM) XF ($CF_3CFHCFHCF_2CF_3$) and Freon(TM) 113 (CF_2ClCCl_2F).

30   ## Photoresists

The photoresists of this invention are comprised of a copolymer (as described supra) and at least one photoactive component (PAC, discussed infra). The photoresists can either be positive-working or negative-working. Positive-working photoresists are preferred. These photoresists can optionally comprise

35   dissolution inhibitors and/or other additional components. Examples of additional components which can be added include, but are not limited to, resolution enhancers, adhesion promoters, residue reducers, coating aids, plasticizers, and T_g (glass transition temperature) modifiers.

A typical photoresist formulation comprises the copolymer, as described herein, comprising the first repeat unit and the second repeat unit, solvent and a photoactive component which are usually combined and mixed together, typically, at ambient temperature. Illustrative, nonlimiting solvents which may be used include cyclohexanone, 2-heptanone, 1,2-bis(1,1,2,2-tetrafluoroethoxy)ethane ($HCF_2CF_2OCH_2CH_2OCF_2CF_2H$), or mixtures of two or more of the foregoing solvents.

A cosolvent which facilitates the film forming capabilities of a photoresist formulation containing the copolymer of this invention can be used. Illustratively, in one embodiment a fluorinated compound, 1,2-bis(1,1,2,2-tetrafluoroethoxy)ethane, having the structure $HCF_2CF_2OCH_2CH_2OCF_2CF_2H$ is a suitable cosolvent.

<u>Photoactive Component (PAC)</u>

The compositions of this invention contain at least one photoactive component (PAC) that usually is a compound that affords either acid or base upon exposure to actinic radiation. If an acid is produced upon exposure to actinic radiation, the PAC is termed a photoacid generator (PAG). If a base is produced upon exposure to actinic radiation, the PAC is termed a photobase generator (PBG).

Suitable photoacid generators for this invention include, but are not limited to, 1) sulfonium salts (structure I), 2) iodonium salts (structure II), and 3) hydroxamic acid esters, such as structure III.
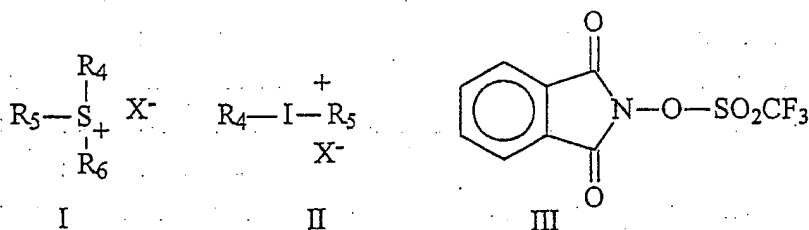
In structures I-II, R_4-R_6 are independently substituted or unsubstituted aryl or substituted or unsubstituted C_1-C_{20} alkylaryl (aralkyl). Representative aryl groups include, but are not limited to, phenyl and naphthyl. Suitable substituents include, but are not limited to, hydroxyl (-OH) and C_1-C_{20} alkyloxy (e.g., $C_{10}H_{21}O$). The anion X- in structures I-II can be, but is not limited to, SbF_6^- (hexafluoroantimonate), $CF_3SO_3^-$ (trifluoromethylsulfonate = triflate), and $C_4F_9SO_3^-$ (perfluorobutylsulfonate).

Protective Groups for Removal by PAC Catalysis

A copolymer of this invention contains, in the second repeat unit, and, optionally, in one or more other repeat unit(s), one or more acid groups or protected acid groups (e.g., protected carboxylic acid groups or protected

5   fluoroalcohol groups) that can yield, by catalysis of acids generated photolytically from photoactive compounds (PACs), hydrophilic acid groups which enable development of resist coatings. (A protected acid group is an acid group that is protected with a protecting group.) A given protected acid group is one that is normally chosen on the basis of its being acid labile, such that when photoacid is

10   produced upon imagewise exposure, the acid will catalyze deprotection and production of hydrophilic acid groups that are at this point unprotected and which are necessary for development under aqueous conditions. In addition, copolymers may also contain one or more acid groups that are not protected. The copolymers may contain none, some, or all acid groups that is/are protected. Photoresists

15   comprised of the copolymers of this invention can be heated to promote deprotection necessary for image formation. An acid group when deprotected affords free acid that enhances the solubility, swellability, and/or dispersibility in aqueous environments of the copolymer to which the acid group is bonded.

Nonlimiting examples of components having protected acid groups that

20   yield an acid group as the hydrophilic group upon exposure to photogenerated acid include A) esters capable of forming, or rearranging to, a tertiary cation, B) esters of lactone, C) acetal esters, D) β-cyclic ketone esters, E) α-cyclic ether esters, F) MEEMA (methoxy ethoxy ethyl methacrylate) and other esters which are easily hydrolyzable because of anchimeric assistance, G) carbonates formed

25   from a fluorinated alcohol and a tertiary aliphatic alcohol. Some specific , examples in category A) are t-butyl ester, t-amyl ester, 2-methyl-2-adamantyl ester, and isobornyl ester. Some specific examples in category B) are γ-butyrolactone-3-yl, γ-butyrolactone-2-yl, mavalonic lactone, 3-methyl-γ-butyrolactone-3-yl, 3-tetrahydrofuranyl, and 3-oxocyclohexyl. Some specific

30   examples in category C) are 2-tetrahydropyranyl, 2-tetrahydrofuranyl, and 2,3-propylenecarbonate-1-yl. Additional examples in category C) include various esters from addition of vinyl ethers, such as, for example, ethoxy ethyl vinyl ether, methoxy ethoxy ethyl vinyl ether, and acetoxy ethyl vinyl ether.

Examples of components having protected acid groups that yield an acid

35   as the hydrophilic group upon exposure to photogenerated acid or base include, but are not limited to, t-butoxycarbonyl (t-BOC), t-butyl ether, and 3-cyclohexenyl ether.

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The acid group or protected acid group may also be derived from a fluoroalcohol or fluoroether. One or more of the first repeat unit, the second repeat unit, the third repeat unit or another component may be derived from at least one ethylenically unsaturated compound containing a fluoroalcohol or

5   fluoroether group having the structure:

$$-C(R_f)(R_f')OR_x$$

wherein R_f and R_f' are the same or different fluoroalkyl groups of from 1 to about

10   10 carbon atoms or taken together are $(CF_2)_n$ wherein n is 2 to 10, and R_x is a hydrogen atom or a C_3-C_6 -secondary- or tertiary-alkyl group. A tertiary-alkyl group is preferred.

In one embodiment of the invention, the second repeat unit can be derived from any one or more of the foregoing acid groups or protected acid groups or the

15   second repeat unit can be derived from a tertiary-alkyl acrylates or tertiary-alkyl methacrylates, wherein the alkyl group contains from four to about ten carbon atoms. Tertiary-alkyl acrylates are more preferred. The most preferred monomer comprised of a protected acid group is tertiary-butyl acrylate (tBA).

In this invention, often, but not always, the components having protected

20   acid groups are repeat units having protected acid groups that have been incorporated in the base copolymer. Frequently the protected acid groups are present in one or more monomer(s) that are copolymerized to form a given copolymer of this invention. Alternatively, in this invention, a copolymer can be formed by copolymerization with an acid-containing monomer and then

25   subsequently the acid group can be partially or wholly converted by appropriate means to derivatives having protected acid groups. As one specific example, a copolymer of HFIB/tBA/VF2 (copolymer containing hexafluoroisobutylene, t-butyl acrylate, and vinylidene fluoride) is a copolymer within the scope of the invention having t-butyl ester groups as protected-acid groups.

30   Dissolution Inhibitors and Additives

Various dissolution inhibitors can be utilized in this invention. Ideally, dissolution inhibitors (DIs) for Deep and vacuum UV resists (e.g., 157 or 193 nm resists) should be designed/chosen to satisfy multiple needs including dissolution inhibition, plasma etch resistance, and adhesion behavior of resist compositions

35   comprising a given DI additive. Some dissolution inhibiting compounds also serve as plasticizers in resist compositions.

A variety of bile-salt esters (i.e., cholate esters) are particularly useful as DIs in the compositions of this invention. Bile-salt esters are known to be

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effective dissolution inhibitors for deep UV resists, beginning with work by
Reichmanis et al. in 1983. (E. Reichmanis et al., "The Effect of Substituents on
the Photosensitivity of 2-Nitrobenzyl Ester Deep UV Resists", *J. Electrochem.
Soc.* 1983, 130, 1433-1437.) Bile-salt esters are particularly attractive choices as

5   DIs for several reasons, including their availability from natural sources, their
possessing a high alicyclic carbon content, and particularly for their being
transparent in the Deep and vacuum UV region of the electromagnetic spectrum
(e.g., typically they are highly transparent at 193 nm). Furthermore, the bile-salt
esters are also attractive DI choices since they may be designed to have widely

10   ranging hydrophobic to hydrophilic compatibilities depending upon hydroxyl
substitution and functionalization.

Representative bile-acids and bile-acid derivatives that are suitable as
additives and/or dissolution inhibitors for this invention include, but are not
limited to, those illustrated below, which are as follows: cholic acid (IV),

15   deoxycholic acid (V), lithocholic acid (VI), t-butyl deoxycholate (VII), t-butyl
lithocholate (VIII), and t-butyl-3-α-acetyl lithocholate (IX). Bile-acid esters,
including compounds VII-IX, are preferred dissolution inhibitors in this invention.

20 .
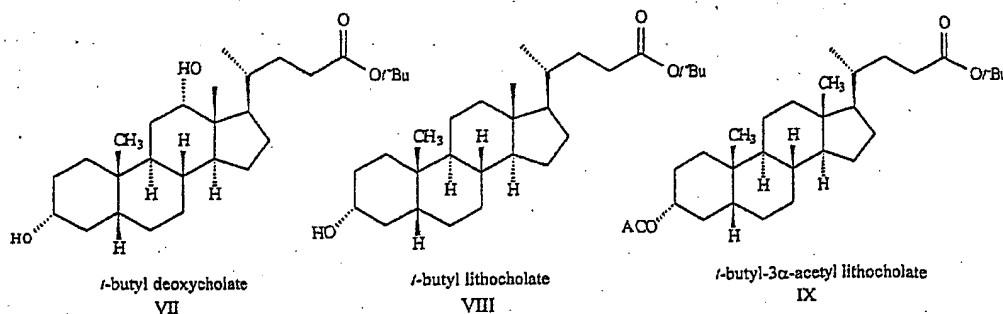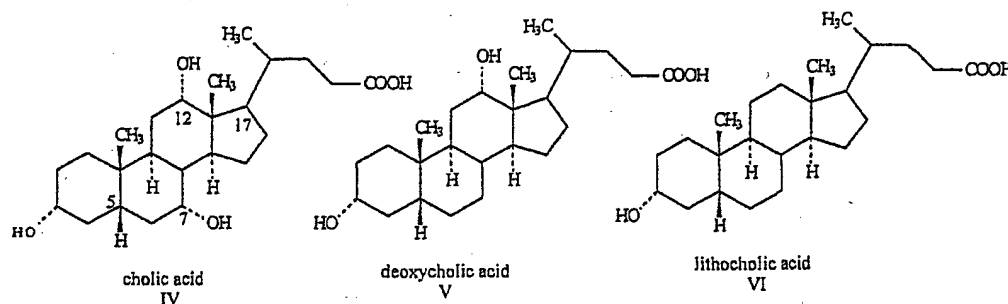
Components for Negative-Working Photoresist Embodiment

Some embodiments of this invention are negative-working photoresists.
25   These negative-working photoresists comprise at least one binder copolymer
comprised of acid-labile groups and at least one photoactive component that

affords photogenerated acid. Imagewise exposure of the resist affords
photogenerated acid which converts the acid-labile groups to polar groups (e.g.,
conversion of ester group (less polar) to acid group (more polar)). Development
is then done in an organic solvent or critical fluid (having moderate to low

5   polarity), which results in a negative-working system in which exposed areas
remain and unexposed areas are removed.

A variety of different crosslinking agents can be employed as required or
optional photoactive component(s) in the negative-working compositions of this
invention. (A crosslinking agent is required in embodiments that involve

10   insolubilization in developer solution as a result of crosslinking, but is optional in
preferred embodiments that involve insolubilization in developer solution as a
result of polar groups being formed in exposed areas that are insoluble in organic
solvents and critical fluids having moderate/low polarity).

<u>Other Components</u>

15   The compositions of this invention can contain optional additional
components. Examples of additional components which can be added include, but
are not limited to, resolution enhancers, adhesion promoters, residue reducers,
coating aids, surfactants, plasticizers, and T_g (glass transition temperature)
modifiers.

20   <u>Process Steps</u>

<u>Imagewise Exposure</u>

The photoresist compositions of this invention are sensitive in the
ultraviolet region of the electromagnetic spectrum and especially to those
wavelengths $\leq$365 nm. Imagewise exposure of the resist compositions of this

25   invention can be done at many different UV wavelengths including, but not
limited to, 365 nm, 248 nm, 193 nm, 157 nm, and lower wavelengths. Imagewise
exposure is preferably done with ultraviolet light of 248 nm, 193 nm, 157 nm, or
lower wavelengths, more preferably it is done with ultraviolet light of 193 nm,
157 nm, or lower wavelengths, and most preferably, it is done with ultraviolet

30   light of 157 nm or lower wavelengths. Imagewise exposure can either be done
digitally with a laser or equivalent device or non-digitally with use of a
photomask. Suitable laser devices for imaging of the compositions of this
invention include, but are not limited to, an argon-fluorine excimer laser with UV
output at 193 nm, a krypton-fluorine excimer laser with UV output at 248 nm, and

35   a fluorine (F2) laser with output at 157 nm. These excimer lasers could be used
for digital imaging, but they are also the basis for non-digital imaging using
photomasks in optical steppers. Optical steppers for 248 nm can use lamps or KrF
excimer laser light sources, and at 193 and 157nm the light source is an excimer

laser, 193nm = ArF and 157nm = F2 excimer laser. Since, as discussed supra, use of UV light of lower wavelength for imagewise exposure corresponds to higher resolution (lower resolution limit), the use of a lower wavelength (e.g., 193 nm or 157 nm or lower) is generally preferred over use of a higher wavelength (e.g.,

5   248 nm or higher).

Development

The copolymers of this invention can be formulated as a positive resist wherein the areas exposed to UV light become sufficiently acidic to be selectively washed out with aqueous base. Sufficient acidity is imparted to the copolymers

10   by acid or protected acid (which can be 100% in protected form prior to exposure provided deprotection occurs during exposure to afford sufficient free acid to provide for development) such that aqueous development is possible using a basic developer such as sodium hydroxide solution, potassium hydroxide solution, or tetramethylammonium hydroxide solution. In this invention, a given copolymer

15   for aqueous processability (aqueous development) in use is typically a carboxylic acid-containing and/or fluoroalcohol-containing copolymer (after exposure) containing at least one free carboxylic acid group and/or fluoroalcohol group. The level of acid groups (e.g., free carboxylic acid or fluoroalcohol groups) is determined for a given composition by optimizing the amount needed for good

20   development in aqueous alkaline developer.

When an aqueous processable photoresist is coated or otherwise applied to a substrate and imagewise exposed to UV light, the copolymer of the photoresist must have sufficient protected acid groups and/or unprotected acid groups so that when exposed to UV the exposed photoresist will become developable in basic

25   solution. In case of a positive-working photoresist layer, the photoresist layer will be removed during development in portions which are exposed to UV radiation but will be substantially unaffected in unexposed portions during development by aqueous alkaline liquids such as wholly aqueous solutions containing 0.262 N tetramethylammonium hydroxide (with development at 25°C usually for less than

30   or equal to 120 seconds) or 1% sodium carbonate by weight (with development at a temperature of 30°C usually for less than 2 or equal to 2 minutes). In case of a negative-working photoresist layer, the photoresist layer will be removed during development in portions which are unexposed to UV radiation but will be substantially unaffected in exposed portions during development using either a

35   critical fluid or an organic solvent.

A critical fluid, as used herein, is one or more substances heated to a temperature near or above its critical temperature and compressed to a pressure near or above its critical pressure. Critical fluids in this invention are at least at a

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temperature that is higher than 15°C below the critical temperature of the fluid and are at least at a pressure higher than 5 atmospheres below the critical pressure of the fluid. Carbon dioxide may be used for the critical fluid in the present invention. Various organic solvents can also be used as developer in this

5   invention. These include, but are not limited to, halogenated solvents and non-halogenated solvents. Halogenated solvents are preferred and fluorinated solvents are more preferred.

<div align="center">GLOSSARY</div>

<div align="center">Analytical/Measurements</div>

10	δ	NMR chemical shift measured in the indicated solvent
	g	gram
	NMR	Nuclear Magnetic Resonance
	^{1}H NMR	Proton NMR
15	^{13}C NMR	Carbon-13 NMR
	s	singlet
	m	multiplet
	mL	milliliter(s)
	mm	millimeter(s)
20	n	Index of Refraction
	T_g	Glass Transition Temperature
	M_n	Number-average molecular weight of a given copolymer determined by gel permeation chromatography using polystyrene standard
25	M_w	Weight-average molecular weight of a given copolymer determined by gel permeation chromatography using polystyrene standard
	Absorbance	A = absorbance of a sample = $\log_{10}(1/T)$, where T = transmittance as defined below.
30	Optical absorbance per micron (Absorbance per micron)	$A/\mu m = A/t$, where A = optical absorbance and t = film thickness in microns.
35	Transmittance	Transmittance, T, = ratio of the radiant power transmitted by a sample to the radiant power incident on the sample and is measured for a specified wavelength λ (e.g., nm).

Chemicals/Monomers

AIBN	2,2'-azobisisobutyronitrile
	Aldrich Chemical Co., Milwaukee, WI
CFC-113	1,1,2-Trichlorotrifluoroethane
	(E. I. du Pont de Nemours and Company,
	Wilmington, DE)
DFIH	Decafluroisohexylene =
	2-perfluoroethyl-3,3,4,4,4-pentafluoro-1-butene
HFIB	Hexafluoroisobutylene =
	2-trifluoromethyl-3,3,3-trifluoro-1-propene
NB	Norbornene = Bicyclo[2.2.1]hept-2-ene
	Aldrich Chemical Co., Milwaukee, WI
THF	Tetrahydrofuran
	Aldrich Chemical Co., Milwaukee, WI
tBA	Tertiary-Butyl acrylate
Vazo® 52	2,4-Dimethyl-2,2'-azobis(pentanenitrile)
	(E. I. du Pont de Nemours and Company,
	Wilmington, DE)
Vazo® 67	2,2'-Azobis(2-methyl butyronitrile)
	(E. I. du Pont de Nemours and Company,
	Wilmington, DE)
PGMEA	Propylene glycol methyl ether acetate
	Aldrich Chemical Co., Milwaukee, WI

SELECTED STRUCTURES

tBA: $CH_2=CHCOOC(CH_3)_3$
DP or "HFPO": $CF_3CF_2CF_2OCF(CF_3)(C=O)OO(C=O)CF(CF_3)OCF_2CF_2CF_3$
HFIB: $CH_2=C(CF_3)_2$
Vertrel™ XF: $CF_3CFHCFHCF_2CF_3$
VF: $CH_2=CHF$
VF2: $CH_2=CF_2$
VAc: $CH_2=CHO(C=O)CH_3$

Ultraviolet

UV	Ultraviolet region of the electromagnetic
	spectrum which ranges from 10 nanometers to
	390 nanometers

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	Extreme UV (EUV)	Region of the electromagnetic spectrum in the ultraviolet that ranges from 10 nanometers to 30 nanometers
5	Vacuum UV (VUV)	Region of the electromagnetic spectrum in the ultraviolet that ranges from 30 nanometers to 200 nanometers
	Deep UV	Region of the electromagnetic spectrum in the ultraviolet that ranges from 200 nanometers to 300 nanometers
10	Near UV	Region of the electromagnetic spectrum in the ultraviolet that ranges from 300 nanometers to 390 nanometers

<u>Copolymers</u>

15	P(A/B/C) X/Y/Z	Copolymer from copolymerization of A, B, and C containing X molar parts of repeat units derived from A, Y molar parts of repeat units derived from B, and Z molar parts of repeat units derived from C

<u>EXAMPLES</u>

20   Unless otherwise specified, all temperatures are in degrees Centigrade, all mass measurements are in grams, and all percentages, with the exception of percentages of repeat units derived from comonomers, are weight percentages. All parts and percentages of repeat units derived from monomers present in the copolymers of this invention are expressed in molar parts and mole percentages,

25   respectively, unless otherwise indicated. All molecular weight determinations were made by GPC using polystyrene standard.

        Most often, copolymer compositions were estimated by carbon/hydrogen analysis in which case compositions were believed accurate within 10 to 15 mole percent. As an alternate method, copolymer compositions were occasionally

30   determined by Carbon-13 NMR in which case compositions were believed accurate within 5 to 10 mole percent.

        The optical absorbance per micron of a film containing the copolymer of this invention was determined by forming a film of the copolymer onto a substrate. This was accomplished by the standard procedure of spin coating a

35   solution of the copolymer of this invention onto a CaF_2 substrate and followed by drying the coated substrate. The optical absorbance was measured per micron of film thickness. The VUV transmission of each CaF_2 substrate was measured prior to coating of the substrate. Then the VUV transmission of the coated substrate

was measured, and using the measured film thickness, the optical absorbance per micron for the film, as a function of wavelength, was determined, which included the values of the optical absorbance per micron for wavelengths of 157 nm and 193 nm.

5   The VUV transmission of the CaF$_2$ substrates and the films on the CaF$_2$ substrates were measured with a VUV Spectrophotometer using a laser plasma light source, a sample chamber capable of both transmission and reflectance measurements, a 1 meter monochromator and a sodium salicylate phosphor coated 1024 element photodiode detector. This procedure is discussed in greater detail in

10   R. H. French, "Laser-Plasma Sourced, Temperature Dependent VUV Spectrophotometer Using Dispersive Analysis", *Physica Scripta*, 41, 4, 404-8, (1990).). The VUV transmission was compared to, and if necessary scaled to match, the UV transmission of the samples measured using a Perkin Elmer Lambda 9 UV/visible spectrophotometer (Perkin Elmer Analytical Instruments,

15   761 Main Avenue, Norwalk CT 06859).

The VUV transmission of the CaF$_2$ substrates and the copolymer films on the CaF$_2$ substrates for Examples 8, 9 and 10 were measured with a VUV Ellipsometer capable of transmission and reflectance measurements. This VUV Ellipsometer uses a deuterium and Xenon lamp light sources, a double

20   monochromator, an AutoRetarder for greater accuracy and a photomultiplier and a photodiode detector.

The analytical procedures and their accuracy, the VUV spectrophotometer and the VUV Ellipsometry are discussed in greater detail in R. H. French, R. C. Wheland, D. J. Jones, J. N. Hilfiker, R. A. Synowicki, F. C. Zumsteg, J. Feldman,

25   A. E. Feiring, "Fluoropolymercopolymers for 157 nm Lithography: Optical Properties from VUV Absorbance and Ellipsometry Measurements", Optical Microlithography XIII, SPIE Vol. 4000, edited by C. J. Progler, 1491-1502 (2000).

More specifically, all optical absorbance per micron measurements were
30   made using the procedure listed below.

Samples were first spin-coated on silicon wafers on a Brewer Cee (Rolla, MO), Spincoater/Hotplate model 100CB.

a) Two to four silicon wafers were spun at different speeds (e.g., 2000, 3000, 4000, 6000 rpm) to obtain differing film thickness and the coated
35   wafers were subsequently baked at 80°C for 2 min. The dried films were then measured for thickness on a Filmetrics F20 Film Measurement System (Filmetrics, Inc., 7675 Dagget St., Suite 140, San Diego, CA 92111-2255) or on a Dektak Stylus Profiler Model IIA, (Veeco Metrology Group, 112 Robin Hill

Road, Santa Barbara, CA 93117). Spin speeds were then selected from this data
to spin the CaF$_2$ substrates for the spectrometer measurement.

      b) CaF$_2$ substrates (1/2" dia. x 0.040" thick) were selected and the
transmission of the substrate determined on the VUV Spectrophotometer or the

5   VUV Ellipsometer.

      c) Spin speed was selected from the silicon wafer data from a) to
spin the sample material onto the CaF$_2$ reference substrates (e.g., 2000 and
6000 rpm) to achieve the desired film thickness. It was baked at 80°C for 2 min.
and the transmission of the film on the substrate was collected on the VUV

10   Spectrometer or the VUV Ellipsometer.

      The optical absorbance per micron, which is the absorbance A per micron
of film thickness, is defined in Equation 1 as the base 10 logarithm of the ratio of
the substrate transmission divided by the transmission of the sample consisting of
the film sample on its substrate, this quantity divided by the film thickness t.

15   Equation 1. $A/\mu m_{film} = A_{film}/t_{film} = \log_{10}\{T_{substrate}/T_{sample}\}/t_{film}$
Wherein:

$A/\mu m_{film}$ is the optical absorbance per micron in units of μm^{-1} of a given film
determined for a specified wavelength of light.

A_{film} is the absorbance (unitless) of a given film determined for a specified

20   wavelength of light.

$T_{substrate}$ is the transmittance (unitless) of a substrate (e.g. a calcium fluoride
plate) determined for a specified wavelength of light.

T_{sample} is the transmittance (unitless) of a sample of a given film and a substrate
determined for a specified wavelength of light.

25   t_{film} is thickness of a given film in microns.

      In this manner, the optical absorbance per micron $A/\mu m$ has units of
inverse microns (or 1/micron, where a micron, is a micrometer or μm of film
thickness). The absorbance/micron of films were measured for films spun coated
on to CaF$_2$ substrates using the above-described methods. The VUV transmission

30   of each CaF$_2$ substrate was measured prior to the spin coating of the film. Then
the VUV transmission of the film on that particular CaF$_2$ substrate was measured,
and using the measured film thickness (reported in Table 1) and equation 1, the
values of the absorbance/micron for the copolymers, as a function of wavelength
were determined, and the values of the absorbance/micron for wavelengths of

35   157 nm and 193 nm are tabulated in Table 2.

Table 2. Optical Absorbance per Micron (μm^{-1}) of Base Resins and Formulated Resists					
Example #	Base Resin Name	A/μm (157nm)	A/μm (193nm)	Thick. (Å)	Spin Speed (Rpm)
1	P(HFIB/VF/tBA)	2.89	0.01	866	6k
2	P(HFIB/VF/tBA)	3.64	0.08	1606	6k
3	P(HFIB/VF2/tBA)	2.12	0.07	838	6k
4	P(HFIB/VF2/tBA)	1.57	0.15	760	6k
5	P(HFIB/Vac/tBA)	2.16	0.03	763	6k
6	P(HFIB/tBA)				
7	P(HFIB/VF2/tBA)	4.33	0.13	1584	6k
8	P(HFIB/VF/tBMA)	4.69	0.20	7930	2k
8	P(HFIB/VF2/tBMA) Resist 8B	5.37	0.83	1108	6k
9	P(HFIB/VF/tBMA)	4.40	0.22	10003	2k
9	P(HFIB/VF/tBMA) Resist 9A	5.71	0.88	2284	6k
9	P(HFIB/VF/tBMA) Resist 9B	6.43	1.08	1188	6k
10	P(HFIB/tBA)	3.74	0.12	9510	2k
10	P(HFIB:tBA) Resist 10B	5.43	0.81	1160	6k

Image Formation/Lithographic Evaluation

With respect to photoresist exposure, the term "clearing dose" indicates the minimum exposure energy density (e.g., in units of mJ/cm^2) to enable a given photoresist film, following exposure, to undergo development.

EXAMPLE 1

Poly(Hexafluoroisobutylene/Vinyl Fluoride/t-Butyacrylate) (0.25/0.25/0.5)

Copolymer Synthesis

A 210 ml stainless steel autoclave was loaded with 15 ml CF2ClCCl2F and 14 ml of t-butylacrylate (tBA). After chilling to less than -20°C, 20 ml of about 0.18 M DP in Vertrel™ XF were added. The autoclave was sealed, chilled, evacuated, and 64 g of hexafluoroisobutylene (HFIB) and 4 g of vinyl fluoride (VF) added. The reaction mixture was shaken overnight (about 21 hours) at ambient temperature, reaching a peak of 34.9 psi (241 kPa) at 22.2°C. The fluid reaction mixture was evaporated to dryness, put under pump vacuum for a week, and then dried in a 65-90°C vacuum oven for 7 hours. This gave 14 g of brittle solid, which was characterized below.

Calc. (HFIB)$_{0.25}$(VF)$_{0.25}$(tBA)$_{0.5}$: 51.50C; 6.27H

Found: 51.25C; 6.24H

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<u>Optical Absorbance per Micron Determination</u>

A solution of this copolymer [P(HFIB/VF/tBA) (0.25/0.25/0.5)] was
spin coated from 2-heptanone at a spin speed of 6000 rpm onto CaF_2 substrates to
produce copolymer film of 866 angstroms thickness. VUV absorbance

5   measurements were then used to determine the absorbance per micron as
explained supra.

The optical absorbance per micron in units of inverse microns for
P(HFIB/VF/tBA) versus wavelength lambda (λ) in units of nanometers is shown
in Figure 3. The optical absorbance per micron at 157 nm determined from the

10   copolymer film is 2.89/micron. The optical absorbance per micron at 193 nm
determined from the copolymer film is 0.01/micron.

<u>Image Generation/Lithographic Evaluation</u>

The following solution was prepared and magnetically stirred overnight at
ambient temperature.

15 | Component | Wt. (gm) |
|---|---|
| HFIB/VF/tBA copolymer (0.25/0.25/0.5) | |
| as described in this example. | 0.294 |
| Cyclohexanone | 2.586 |
| 5% (wt) solution of triphenylsulfonium triflate | |
20 | dissolved in cyclohexanone which had been | |
| filtered through a 0.45 μ PTFE syringe filter. | 0.120 |

A thin film was prepared for lithographic evaluation by spin coating the
above formulation on a 4 inch (10.2 cm) diameter Type "P", <100> orientation,
silicon wafer. Spin coating was done using a Brewer Science Inc. Model-100CB

25   combination spin coater/hotplate. Development was performed on a Litho Tech
Japan Co. Resist Development Analyzer (Model-790).

The wafer was prepared by depositing 6 ml of hexamethyldisilazane
(HMDS) primer and spinning at 1000 rpm for 5 sec. and then 3500 rpm for
10 sec. Then 6 ml of the above solution, after filtering through a 0.45 μm PTFE

30   syringe filter, was deposited and spun at 3000 rpm for 60 seconds and baked at
120°C for 60 seconds.

248 nm imaging was accomplished by exposing the coated wafer to light
obtained by passing broadband UV light from an ORIEL Model-82421 Solar
Simulator (1000 watt) through a 248 nm interference filter which passes about

35   30% of the energy at 248 nm. Exposure time was 30 seconds, providing an
unattenuated dose of 20.5 mJ/cm2. By using a mask with 18 positions of varying
neutral optical density, a wide variety of exposure doses were generated. After
exposure, the exposed wafer was baked at 120°C for 120 seconds.

The wafer was developed in aqueous tetramethylammonium hydroxide (TMAH) solution (ONKA NMD-3, 2.38% TMAH solution). Development time was 60 sec. A positive image was produced on the wafer with a clearing dose of approximately 21 mJ/cm^2.

5   EXAMPLE 2

Poly(Hexafluoroisobutylene/Vinyl Fluoride/t-Butyacrylate) (0.22/0.39/0.39)

Copolymer Synthesis

A 210 ml stainless steel autoclave was loaded with 15 ml CF$_2$ClCCl$_2$F and 14 ml of t-butylacrylate (tBA). After chilling to less than -20°C, 20 ml of

10   about 0.16 M DP in Vertrel™ XF were added. The autoclave was sealed, chilled, evacuated, and 32 g of hexafluoroisobutylene and 5 g of vinyl fluoride added. The reaction mixture was shaken overnight (about 12 hours) at ambient temperature, reaching a peak of 207 psi (1430 kPa) at 24.8°C. The fluid reaction mixture was evaporated to dryness, put under pump vacuum for 18 hours, and

15   then dried in 75°C vacuum oven for 30 hours. This gave 17 g of brittle solid, which was characterized below.

DSC analysis indicated a Tg (glass transition temperature) at 46°C (first heat, N$_2$, 10°C/min).

Calc. (HFIB)$_{0.22}$(VF)$_{0.39}$(tBA)$_{0.39}$: 50.74C; 6.11H

20   Found: 50.58C; 6.15H

Optical Absorbance per Micron Determination

Solutions of P(HFIB/VF/tBA) (0.22/0.39/0.39) were spin coated from ethyl lactate at spin speeds of 6000 rpm onto CaF$_2$ substrates to produce films of 1606 angstroms thickness. VUV absorbance measurements were then used to

25   determine the optical absorbance per micron.

The optical absorbance per micron in units of inverse microns for P(HFIB/VF/tBA) (0.22/0.39/0.39) versus wavelength lambda (λ) in units of nanometers is shown in Figure 4. The optical absorbance per micron at 157 nm determined from the film is 3.64/micron. The optical absorbance per micron at

30   193 nm determined from the film is 0.08/micron.

Image Generation/Lithographic Evaluation

The following solution was prepared and magnetically stirred overnight at ambient temperature.

Component	Wt. (gm)
P(HFIB/VF/tBA) copolymer (0.22/0.39/0.39) as described in this example.	0.234
Cyclohexanone	2.586.
t-Butyl Lithocholate	0.060
5% (wt) solution of triphenylsulfonium triflate dissolved in cyclohexanone which had been filtered through a 0.45µ PTFE syringe filter.	0.120

This solution was subjected to the image generation/lithographic evaluation procedure as described in Example 1. A positive image was produced on the wafer with a clearing dose of approximately 6.9 mJ/cm^2.

EXAMPLE 3

Poly(Hexafluoroisobutylene/Vinylidene Fluoride/t-Butyacrylate) (0.25/0.2/0.55)

Copolymer Synthesis

A 210 ml stainless steel autoclave was loaded with 15 ml Vertrel™ XF and 10 ml of t-butylacrylate (tBA). After chilling to less than -20°C, 20 ml of about 0.18 M DP in Vertrel™ XF were added. The autoclave was sealed, chilled, evacuated, and 32 g of hexafluoroisobutylene and 8 g of vinylidene fluoride added. The reaction mixture was shaken overnight (about 20 hours) at ambient temperature, reaching a peak of 79 psi (540 kPa) at 20.6°C. The fluid reaction mixture was evaporated to dryness, put under pump vacuum for a week, and dried for 7 hours in a 65-90°C vacuum oven. This gave 13 g of brittle solid, which was characterized as given below.

Calc. $(HFIB)_{0.25}(VF2)_{0.20}(tBA)_{0.55}$: 50.72C; 6.08H

Found: 50.66; 6.13H

Optical Absorbance per Micron Determination

Solutions of this copolymer [P(HFIB/VF2/tBA) (0.25/0.2/0.55)] were spin coated from 2-heptanone at spin speeds of 6000 rpm onto CaF$_2$ substrates to produce copolymer films of 838 angstroms thickness. VUV absorbance measurements were then used to determine the optical absorbance per micron.

The optical absorbance per micron in units of inverse microns for P(HFIB:VF2:tBA) (0.25/0.2/0.55) versus wavelength lambda (λ) in units of nanometers is shown in Figure 5. The optical absorbance per micron at 157 nm determined from the copolymer film is 2.12/micron. The optical absorbance per micron at 193 nm determined from the copolymer film is 0.07/micron.

Image Generation/Lithographic Evaluation

The following solution was prepared and magnetically stirred overnight at ambient temperature.

Component	Wt. (gm)
HFIB/VF2/tBA copolymer (0.25/0.2/0.55)	
as described in this example.	0.234
Cyclohexanone	2.586.
t-Butyl Lithocholate	0.060

5

5% (wt) solution of triphenylsulfonium triflate

dissolved in cyclohexanone which had been

filtered through a 0.45µ PTFE syringe filter.   0.120

This solution was subjected to the image generation/lithographic

10   evaluation procedure as described in Example 1. A positive image was produced

on the wafer with a clearing dose of approximately 21 mJ/cm^2.

EXAMPLE 4

Poly(Hexafluoroisobutylene/Vinylidene Fluoride/t-Butylacrylate)

(0.29/0.29/0.42)

15   Copolymer Synthesis

A 210 ml stainless steel autoclave was loaded with 15 ml Vertrel™ XF

and 5 ml of t-butylacrylate (tBA). After chilling to less than -20°C, 20 ml of

about 0.18 M DP in Vertrel™ XF were added. The autoclave was sealed, chilled,

evacuated, and 32 g of hexafluoroisobutylene and 8 g of vinylidene fluoride

20   added. The reaction mixture was shaken overnight (about 20 hours) at ambient

temperature, reaching a peak of 69 psi (470 kPa) at 21.1°C. The fluid reaction

mixture was evaporated to dryness, put under pump vacuum for a week, and dried

for 7 hours in a 65-90°C vacuum oven. This gave 7.7 g of brittle solid, which was

characterized as indicated below.

25   Calc. $(HFIB)_{0.29}(VF2)_{0.29}(tBA)_{0.42}$: 46.74C; 5.18H

Found: 46.59C; 5.30H

Optical Absorbance per Micron Determination

Solutions of P(HFIB:VF2:tBA) (0.29/0.29/0.42) were spin coated from

2-heptanone at spin speeds of 6000 rpm onto CaF$_2$ substrates to produce

30   copolymer films of 760 angstroms thickness. VUV absorbance measurements

were then used to determine the optical absorbance per micron.

The optical absorbance per micron in units of inverse microns for

P(HFIB/VF2/tBA) (0.29/0.29/0.42) versus wavelength lambda (λ) in units of

nanometers is shown in Figure 6. The optical absorbance per micron at 157 nm

35   determined from the copolymer film is 1.57/micron. The optical absorbance per

micron at 193 nm determined from the copolymer film is 0.15/micron.

Image Generation/Lithographic Evaluation

The following solution was prepared and magnetically stirred overnight at ambient temperature.

Component	Wt. (gm)
HFIB/VF2/tBA copolymer (0.29/0.29/0.42) as described in this example.	0.234
Cyclohexanone	2.586.
t-Butyl Lithocholate	0.060
5% (wt) solution of triphenylsulfonium triflate dissolved in cyclohexanone which had been filtered through a 0.45μ PTFE syringe filter.	0.120

This solution was subjected to the image generation/lithographic evaluation procedure as described in Example 1. A positive image was produced on the wafer with a clearing dose of approximately 12.6 mJ/cm^2.

In a 1:1 ratio poly(hexafluoroisobutylene:vinyl fluoride) has an A/μ = 0.014 at 157 nm. This hexafluoroisobutylene:vinyl fluoride polymer still needs a photochemical switch to perform as a resist but the functionality associated with a photochemical switch such as t-butyl acrylate tends to increase absorption considerably over that of the base polymer. Comparing Examples 1 and 2, poly(hexafluoroisobutylene:vinyl fluoride:t-butylacrylate) was found to have an A/μ of 2.89 and 3.64 at 157 nm. Replacing the vinyl fluoride in Examples 1 and 2 by the alternating monomer vinylidene fluoride in Examples 3 and 4 reduced A/μ to 1.57 and 2.16 at 157 nm. These data demonstrate the advantage of alternating short $(CH_2)_n$ and $(CF_2)_m$ segments in the polymer for increasing transparency.

EXAMPLE 5

Poly(Hexafluoroisobutylene/Vinyl Acetate/t-Butyacrylate) (0.46/0.27/0.27)

Copolymer Synthesis

A 210 ml stainless steel autoclave was loaded with 50 ml Freon™ 113, 4 ml of vinyl acetate, and 9 ml of t-butylacrylate. The tube was chilled to less than -20°C and 20 ml of about 0.18 M DP in Vertrel™ XF added. The autoclave was sealed, chilled, evacuated, and 66 g of hexafluoroisobutylene added. The reaction mixture was shaken overnight (about 20 hours) at ambient temperature, reaching a peak of 10 psi (69 kPa) at 22°C. The fluid reaction mixture was evaporated to dryness, put under pump vacuum for a week, and dried for 7 hours in a 65-90°C vacuum oven. This gave 21 g of brittle solid, which was characterized as indicated below.

Calc. $(HFIB)_{0.46}(VAc)_{0.27}(tBA)_{0.27}$: 43.51C; 4.41H

Found: 43.21C; 4.63H

Optical Absorbance per Micron Determination

Solutions of P(HFIB/VAc/tBA) (0.46/0.27/0.27) were spin coated from 2-heptanone at spin speeds of 6000 rpm onto CaF_2 substrates to produce copolymer films of 763 angstroms thickness. VUV absorbance measurements were then

5 used to determine the optical absorbance per micron.

The optical absorbance per micron in units of inverse microns for P(HFIB/VAc/tBA) (0.46/0.27/0.27) versus wavelength lambda (λ) in units of nanometers is shown in Figure 7. The optical absorbance per micron at 157 nm determined from the copolymer film is 2.16/micron. The optical absorbance per

10 micron at 193 nm determined from the copolymer film is 0.03/micron.

Image Generation/Lithographic Evaluation

The following solution was prepared and magnetically stirred overnight at ambient temperature.

Component	Wt. (gm)
15 HFIB/VAc/tBA copolymer (0.46/0.27/0.27) as described in this example.	0.294
Cyclohexanone	2.586.
5% (wt) solution of triphenylsulfonium triflate dissolved in cyclohexanone which had been 20 filtered through a 0.45µ PTFE syringe filter.	0.120

This solution was subjected to the image generation/lithographic evaluation procedure as described in Example 1. A positive image was produced on the wafer with a clearing dose of approximately 21 mJ/cm^2.

EXAMPLE 6

25   Poly(Hexafluoroisobutylene/t-Butylacrylate) (41/59)

Copolymer Synthesis

A 75 ml stainless steel autoclave was loaded with 7.3 ml of t-butylacrylate (tBA). After chilling to less than -20°C, 20 ml of about 0.18 M DP in Vertrel™ XF were added. The autoclave was sealed, chilled, evacuated, and 33 g of

30 hexafluoroisobutylene was added. The reaction mixture was shaken overnight (about 21 hours) at ambient temperature, reaching a peak of 11 psi (76 kPa) at 21.7°C. The fluid reaction mixture was evaporated to dryness, put under pump vacuum for a week, and dried for 7 hours in a 65-90°C vacuum oven. This gave 9.8 g of solid, which was characterized as indicated below.

35   Calc. $(HFIB)_{0.41}(tBA)_{0.59}$: 48.44C; 5.56H

          Found: 48.59C; 5.65H

Carbon-13 NMR analysis indicated 37.5 mole % of hexafluoroisobutylene and 62.5 mole % of t-butyl acrylate.

28

<u>Image Generation/Lithographic Evaluation</u>

The following solution was prepared and magnetically stirred overnight at ambient temperature.

Component	Wt. (gm)
HFIB/tBA copolymer (0.41/0.59) as described in this example.	0.234
Cyclohexanone	2.586.
t-Butyl Lithocholate	0.060
5% (wt) solution of triphenylsulfonium triflate dissolved in cyclohexanone which had been filtered through a 0.45µ PTFE syringe filter.	0.120

This solution was subjected to the image generation/lithographic evaluation procedure as described in Example 1. A positive image was produced on the wafer with a clearing dose of approximately 14.6 mJ/cm^2.

<div align="center">EXAMPLE 7</div>

<u>Poly(Hexafluoroisobutylene/Vinylidene Fluoride/t-Butyacrylate) (0.18/0.18/0.64)</u>

<u>Copolymer Synthesis</u>

A 240 ml stainless steel autoclave was loaded with 15 ml Vertrel™ XF and 14 ml of t-butylacrylate (tBA). After chilling to less than -20°C, 20 ml of about 0.16 M DP in Vertrel™ XF were added. The autoclave was sealed, chilled, evacuated, and 32 g of hexafluoroisobutylene and 8 g of vinylidene fluoride added. The reaction mixture was shaken overnight (about 20 hours) at ambient temperature, reaching a peak of 74 psi (510 kPa) at 31.7°C. The fluid reaction mixture was evaporated to dryness, put under pump vacuum for 26 hours, and dried for 30 hours in a 75°C vacuum oven. This gave 10 g of glassy solid, which was characterized as indicated below.

Calc. (HFIB)$_{0.18}$(VF2)$_{0.18}$(tBA)$_{0.64}$: 54.14C; 7.02H

Found: 54.13C; 6.94H

<u>Optical Absorbance per Micron Determination</u>

Solutions of P(HFIB/VF2/tBA) (0.18/0.18/0.64) were spin coated from 1,2-bis(1,1,2,2-tetrafluoroethoxy)ethane at spin speeds of 6000 rpm onto CaF$_2$ substrates to produce copolymer films of 1584 angstroms thickness. VUV absorbance measurements were then used to determine the optical absorbance per micron.

The optical absorbance per micron in units of inverse microns for P(HFIB/VF2/tBA) (0.18/0.18/0.64) versus wavelength lambda (λ) in units of nanometers is shown in Figure 8. The optical absorbance per micron at 157 nm

<div align="center">29</div>

determined from this copolymer film is 4.33/micron. The optical absorbance per micron at 193 nm determined from this copolymer film is 0.13/micron.

<div align="center">

EXAMPLE 8

Poly(Hexafluoroisobutylene/Vinylidene Fluoride/t-Butylmethacrylate)

(0.27/0.27/0.46)

</div>

Copolymer Synthesis

A 210 ml autoclave was loaded with 15 ml of Vertrel™ XF and chilled to less than -20°C. The autoclave was further loaded with 5.7 ml of t-butylmethacrylate and 20 ml of about 0.17 M HFPO DP in Vertrel™ XF. The autoclave was sealed, chilled, evacuated, and loaded with 32 g of hexafluoroisobutylene and 8 g of vinylidene fluoride. The reaction mixture was shaken overnight at ambient temperature (about 20 hours) reaching a peak of 61 psi (421 kPa) at 23°C. The fluid reaction mixture was evaporated to dryness and then put under pump vacuum for 1 week giving 7.9 g of product. An elemental analysis sample dried a further 19 hours in a 50°C vacuum oven gave the following results,

Calc. $(HFIB)_{0.27}(VF2)_{0.27}(tBMA)_{0.46}$: 49.93C; 5.92H

Found: 49.74C; 6.02H

Optical Absorbance per Micron Determination of Base Resin

Solutions of P(HFIB/VF2/tBMA) (0.27/0.27/0.46) in $HCF_2CF_2OCH_2CH_2OCF_2CF_2H$ solvent were spin coated from 1,2-bis(1,1,2,2-tetrafluoroethoxy)ethane at spin speeds of 6000 rpm onto CaF_2 substrates to produce copolymer films of 7930 angstroms thickness. VUV absorbance measurements were then used to determine the optical absorbance per micron.

The optical absorbance per micron in units of inverse microns for P(HFIB/VF2/tBMA) (0.27/0.27/0.46) versus wavelength lambda (λ) in units of nanometers is shown as spectrum 8 in Figure 9 The optical absorbance per micron at 157 nm determined from the copolymer film is 4.69/micron. The optical absorbance per micron at 193 nm determined from the copolymer film is 0.20/micron.

Image Generation/Lithographic Evaluation Resist 8A

The following solution (formulated resist 8A) was prepared and magnetically stirred overnight at ambient temperature.

Component	Wt. (gm)
HFIB/VF2/tBMA copolymer (0.27/0.27/0.46) as described in this example.	0.290
Solvent: $HCF_2CF_2OCH_2CH_2OCF_2CF_2H$	2.561
6.82 % (wt) solution of triphenylsulfonium nonaflate	

<div align="center">

30

</div>

dissolved in $HCF_2CF_2OCH_2CH_2OCF_2CF_2H$ which

had been filtered through a 0.45μ PTFE syringe filter.　　　0.150

This solution was subjected to the image generation/lithographic

evaluation procedure as described in Example 1. A positive image was produced

5　　on the wafer with a clearing dose of approximately 7.6 mJ/cm^2.

Image Generation/Lithographic Evaluation For Resist 8B

The following solution (formulated resist 8B) was prepared and magnetically stirred

overnight at ambient temperature.

Component	Wt. (gm)
HFIB/VF2/tBMA copolymer (0.27/0.27/0.46) as described in this example.	0.245
Solvent: 65/35 (wt.) $HCF_2CF_2OCH_2CH_2OCF_2CF_2H$/ /2-heptanone	2.561
t-butyl lithocholate	0.045
6.82 % (wt) solution of triphenylsulfonium nonaflate dissolved in 65/35 (wt.) $HCF_2CF_2OCH_2CH_2OCF_2CF_2H$/ 2-heptanone which had been filtered through a 0.45μ PTFE syringe filter.	0.150

This solution was subjected to the image generation/lithographic

20　　evaluation procedure as described in Example 1. A positive image was produced

on the wafer with a clearing dose of approximately 3.4 mJ/cm^2.

Optical Absorbance per Micron Determination of Copolymer Film of

Formulated Resist 8B

The solution used for image generation/lithographic evaluation was spin

25　　coated from 1,2-bis(1,1,2,2-tetrafluoroethoxy)ethane at a spin speed of 2000 rpm

onto CaF2 substrates to produce copolymer films of 1108 angstroms thickness.

VUV absorbance measurements were then used to determine the optical

absorbance per micron.

The optical absorbance per micron in units of inverse microns for

30　　copolymer film produced from this formulated resist versus wavelength lambda

(λ) in units of nanometers is shown as spectrum 8B in Figure 9. The optical

absorbance per micron at 157 nm determined from the copolymer film is

5.37/micron. The optical absorbance per micron at 193 nm determined from the

copolymer film is 0.83/micron.

EXAMPLE 9

Poly(Hexafluoroisobutylene/Vinylidene Fluoride/t-Butylmethacrylate)

(0.23/0.26/0.51)

Copolymer Synthesis

A 400 ml autoclave was loaded with 30 ml of Vertrel™ XF and chilled to less than -20°C. The autoclave was further loaded with 17 ml of t-butylmethacrylate and 60 ml of about 0.17 M HFPO DP in Vertrel™ XF. The autoclave was sealed, chilled, evacuated, and loaded with 96 g of hexafluoroisobutylene and 24 g of vinylidene fluoride. The reaction mixture was shaken overnight at ambient temperature (about 17 hours) reaching a peak of 114 psi (786 kPa) at 30°C. The fluid reaction mixture was evaporated to dryness and then further dried for 10 days under pump vacuum and for 22 hours in a 75°C vacuum oven giving 19 g of product. Elemental analysis found,

Calc. $(HFIB)_{0.23}(VF2)_{0.26}(tBMA)_{0.51}$: 52.30C; 6.46H

Found: 52.33C; 6.37H

Optical Absorbance per Micron Determination of Base Resin

Solutions of P(HFIB/VF2/tBMA) (0.23/0.26/0.51) in $HCF_2CF_2OCH_2CH_2OCF_2CF_2H$ solvent were spin coated from 1,2-bis(1,1,2,2-tetrafluoroethoxy)ethane at spin speeds of 2000 rpm onto CaF_2 substrates to produce copolymer films of 10003 angstroms thickness. VUV absorbance measurements were then used to determine the optical absorbance per micron.

The optical absorbance per micron in units of inverse microns for P(HFIB/VF2/tBMA) (0.23/0.26/0.51) versus wavelength lambda (λ) in units of nanometers is shown as spectrum 9 in Figure 10. The optical absorbance per micron at 157 nm determined from the copolymer film is 4.40/micron. The optical absorbance per micron at 193 nm determined from the copolymer film is 0.22/micron.

Image Generation/Lithographic Evaluation For Resist 9A

The following solution (formulated resist 9A) was prepared and magnetically stirred overnight at ambient temperature.

Component	Wt. (gm)
HFIB/VF$_2$/tBMA copolymer (0.23/0.26/0.51) as described in this example.	0.290
Solvent: HCF$_2$CF$_2$OCH$_2$CH$_2$OCF$_2$CF$_2$H	2.561
6.82 % (wt) solution of triphenylsulfonium nonaflate dissolved in HCF$_2$CF$_2$OCH$_2$CH$_2$OCF$_2$CF$_2$H which had been filtered through a 0.45μ PTFE syringe filter.	0.150

This solution was subjected to the image generation/lithographic evaluation procedure as described in Example 1. A positive image was produced on the wafer with a clearing dose of approximately 4.3 mJ/cm^2.

Optical Absorbance per Micron Determination of Copolymer Film of

5   Formulated Resist 9A

The solution used for image generation/lithographic evaluation was spin coated from 1,2-bis(1,1,2,2-tetrafluoroethoxy)ethane at a spin speed of 6000 rpm onto CaF2 substrates to produce copolymer films of 2284 angstroms thickness. VUV absorbance measurements were then used to determine the optical

10   absorbance per micron.

The optical absorbance per micron in units of inverse microns for copolymer film produced from this formulated resist versus wavelength lambda (λ) in units of nanometers is shown as spectrum 9A in Figure 10. The optical absorbance per micron at 157 nm determined from the copolymer film is

15   5.71/micron. The optical absorbance per micron at 193 nm determined from the copolymer film is 0.88/micron.

Image Generation/Lithographic Evaluation For Resist 9B

The following solution (formulated resist 9B) was prepared and magnetically stirred overnight at ambient temperature.

20	Component	Wt. (gm)
	HFIB/VF$_2$/tBMA copolymer (0.23/0.26/0.51) as described in this example.	0.245
	Solvent: 65/35 (wt.) HCF$_2$CF$_2$OCH$_2$CH$_2$OCF$_2$CF$_2$H/ /2-heptanone	2.561
25	t-butyl lithocholate	0.045
	6.82-% (wt) solution of triphenylsulfonium nonaflate dissolved in 65/35 (wt.) HCF$_2$CF$_2$OCH$_2$CH$_2$OCF$_2$CF$_2$H/ 2-heptanone which had been filtered through a 0.45μ PTFE syringe filter.	0.150

30   This solution was subjected to the image generation/lithographic evaluation procedure as described in Example 1. A positive image was produced on the wafer with a clearing dose of approximately 5.6 mJ/cm^2.

Optical Absorbance per Micron Determination of Copolymer Film of

Formulated Resist 9B

35   The solution used for image generation/lithographic evaluation was spin coated from 1,2-bis(1,1,2,2-tetrafluoroethoxy)ethane at a spin speed of 6000 rpm onto CaF2 substrates to produce copolymer films of 1188 angstroms thickness.

VUV absorbance measurements were then used to determine the optical absorbance per micron.

The optical absorbance per micron in units of inverse microns for copolymer film produced from this formulated resist versus wavelength lambda (λ) in units of nanometers is shown as spectrum 9B in Figure 10. The optical absorbance per micron at 157 nm determined from the copolymer film is 6.43/micron. The optical absorbance per micron at 193 nm determined from the copolymer film is 1.08/micron.

<u>EXAMPLE 10</u>

Poly(Hexafluoroisobutylene/t-Butylacrylate) (0.44/0.56)

<u>Copolymer Synthesis</u>

An autoclave was chilled to less than -20°C and loaded with 20 ml of about 0.17 M HFPO DP in Vertrel™ XF and 7.3 ml of t-butylacrylate. The autoclave was sealed, chilled, evacuated, and loaded with 100 g of hexafluoroisobutylene. The reaction mixture was shaken overnight at ambient temperature (about 18 hours) reaching a peak of 10 psi (69 kPa) at 24°C. The fluid reaction mixture was evaporated to dryness and then futher dried for 5 days under pump vacuum and for 2 to 3 days in a 50°C vacuum oven giving 7 g of product. Elemental analysis found,

Calc. (HFIB)$_{0.44}$(tBA)$_{0.56}$: 47.23C; 5.28H

Found: 47.15C; 5.06H

<u>Optical Absorbance per Micron Determination of Base Resin</u>

Solutions of P(HFIB/tBA) (0.44/0.56) in $HCF_2CF_2OCH_2CH_2OCF_2CF_2H$ solvent were spin coated at spin speeds of 2000 rpm onto CaF_2 substrates to produce copolymer films of 9510 angstroms thickness. VUV absorbance measurements were then used to determine the optical absorbance per micron.

The optical absorbance per micron in units of inverse microns for P(HFIB/tBA) (0.44/0.56) versus wavelength lambda (λ) in units of nanometers is shown as spectrum 10 in Figure 11. The optical absorbance per micron at 157 nm determined from the copolymer film is 3.74/micron. The optical absorbance per micron at 193 nm determined from the copolymer film is 0.12/micron.

<u>Image Generation/Lithographic Evaluation For Resist 10A</u>

The following solution (formulated resist 10A) was prepared and magnetically stirre overnight at ambient temperature.

Component	Wt. (gm)
HFIB/tBA copolymer (0.44/0.56) as described in this example.	0.290
Solvent: 65/35 (wt.) $HCF_2CF_2OCH_2CH_2OCF_2CF_2H$/	2.561

34

/2-heptanone

6.82 % (wt) solution of triphenylsulfonium triflate

dissolved in $HCF_2CF_2OCH_2CH_2OCF_2CF_2H$ which

had been filtered through a 0.45μ PTFE syringe filter.   0.150

This solution was subjected to the image generation/lithographic
evaluation procedure as described in Example 1. A positive image was produced
on the wafer with a clearing dose of approximately 4.3 mJ/cm².

Image Generation/Lithographic Evaluation For Resist 10B

The following solution (formulated resist 10B) was prepared and magnetically stirre
overnight at ambient temperature.

Component	Wt. (gm)
HFIB/tBA copolymer (0.44/0.56) as described in this example.	0.245
Solvent: $HCF_2CF_2OCH_2CH_2OCF_2CF_2H$	2.561

6.82 % (wt) solution of triphenylsulfonium triflate

dissolved in 65/35 (wt.) $HCF_2CF_2OCH_2CH_2OCF_2CF_2H$/

2-heptanone which had been filtered through a 0.45μ

PTFE syringe filter.   0.150

This solution was subjected to the image generation/lithographic
evaluation procedure as described in Example 1. A positive image was produced
on the wafer with a clearing dose of approximately 4.3 mJ/cm².

Optical Absorbance per Micron Determination of Copolymer Film of
Formulated Resist 10B

The solution used for image generation/lithographic evaluation was spin
coated at a spin speed of 6000 rpm onto CaF2 substrates to produce copolymer
films of 1160 angstroms thickness. VUV absorbance measurements were then
used to determine the optical absorbance per micron.

The optical absorbance per micron in units of inverse microns for
copolymer film produced from this formulated resist versus wavelength lambda
(λ) in units of nanometers is shown as spectrum 10B in Figure 11. The optical
absorbance per micron at 157 nm determined from the copolymer film is
5.43/micron. The optical absorbance per micron at 193 nm determined from the
copolymer film is 0.81/micron.

EXAMPLE 11(Prophetic)

This example illustrates that the compound having the structure of
$HCF_2CF_2OCH_2CH_2OCF_2CF_2H$ is significantly better as a spreading solvent on
silicon in relation to standard solvents (e.g., 2-heptanone).

Solutions are made by dissolving 0.1 g of P(HFIB/VF2/tBMA) (0.23/0.26/0.51) from Example 9 in 1 gram of 2-heptanone and 0.1 g of P(HFIB/VF2/tBMA) (0.23/0.26/0.51) from Example 9 in 1 gram of $HCF_2CF_2OCH_2CH_2OCF_2CF_2H$. Both solutions are spotted on silicon wafers and

5   allowed to air dry. As the solution in 2-heptanone dries, the liquid pool beads up eventually leaving a thick deposit of copolymer about 0.25" in diameter and scattered thin patches copolymer where the solution has drawn back from the wafer surface. In contrast the solution in $HCF_2CF_2OCH_2CH_2OCF_2CF_2H$ dries down to a smooth copolymer film roughly the diameter of the starting liquid pool.

10   Paralleling this better wetting for copolymer in $HCF_2CF_2OCH_2CH_2OCF_2CF_2H$ solvent, the solution in $HCF_2CF_2OCH_2CH_2OCF_2CF_2H$ spin coats to a more attractive and uniform film than the same copolymer in 2-heptanone solvent.

CLAIMS

What is claimed is:

1. A copolymer comprising:

    (a) a first repeat unit derived from at least one fluoroolefin having

5   the structure:

$$(H)(H)C=C(R_1)(R_2)$$
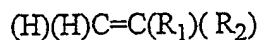
10   wherein R_1 and R_2 are independently selected from the group consisting of C_1-C_3 perfluoroalkyl, or taken together are $(CF_2)_n$ wherein n is 3 to 5; and

    (b) a second repeat unit derived from a first ethylenically unsaturated comonomer comprising an acid group or a protected acid group.

15   2. The copolymer of Claim 1 wherein the second repeat unit is a tertiary-alkyl acrylate or a tertiary-alkyl methacrylate in which the alky group ranges from four to about ten carbon atoms and the first repeat unit is hexafluoroisobutylene or decafluoroisohexylene.

3. The copolymer of Claim 2 wherein the first repeat unit is

20 hexafluoroisobutylene and the second repeat unit is the tertiary-alkyl acrylate.

4. The copolymer of Claim 1 further comprising a third repeat unit derived from a second ethylenically unsaturated comonomer.

5. The copolymer of Claim 4 wherein the third repeat unit is derived from vinyl fluoride, vinylidene fluoride, vinyl acetate, trifluoroethylene,

25 tetrafluoroethylene, 4,5-difluoro-2,2-bis(trifluoromethyl)-1,3-dioxole, 2,2-bis(trifluoromethyl)-1,3-dioxole, vinyl alcohol, 1,3-dioxole-2-one, or maleic anhydride.

6. The copolymer of Claim 1 in which the copolymer further comprises an aliphatic polycyclic functionality.

30   7. The copolymer of Claim 6 wherein the percentage of repeat units of the copolymer containing aliphatic polycyclic functionality ranges from about 1 to about 50 mole percent.

8. The copolymer of Claim 1 further comprising at least one member selected from the group consisting of a carboxylic acid, a fluoroalcohol, and a

35 protected fluoroalcohol.

9. The copolymer of Claim 1 made by a solution polymerization process comprising a solvent and an initiator.

10. The copolymer of Claim 9 in which the solvent is a fluorocarbon, chlorofluorocarbon, chlorofluorohydrocarbon, or hydrofluorocarbon and the initiator is a diacyl peroxide, dimer peroxide, percarbonate, or 2,2'-azobisisobutyronitrile.

5   11. A photoresist comprising the copolymer of Claims 1, 2, 3, 4, 5, 6, 7 or 8.

12. The photoresist of Claim 11 wherein the copolymer has an absorption coefficient of less than 5.0 μm^{-1} at a wavelength of 157 nm.

13. The photoresist of Claim 11 which is a positive-working photoresist.

10   14. The photoresist of Claim 11 wherein the photoactive component is a photoacid generator.

15. The photoresist of Claim 11 wherein the photoresist is developable so as to produce a relief image upon imagewise exposure to ultraviolet radiation having wavelength of <365 nm.

15   16. The photoresist of Claim 11 further comprising a solvent.

17. The photoresist of Claim 16 wherein the solvent is selected from the group consisting of cyclohexanone, 2-heptanone, and $HCF_2CF_2OCH_2CH_2OCF_2CF_2H$.

18. The photoresist of Claim 16 further comprising a cosolvent which

20   facilitates the film forming capabilities of a photoresist formulation.

19. The photoresist of Claim 18 in which the cosolvent is $HCF_2CF_2OCH_2CH_2OCF_2CF_2H$.

20. The photoresist of Claim 11 in which the solvent is 2-heptanone and the cosolvent is $HCF_2CF_2OCH_2CH_2OCF_2CF_2H$.

25   21. The photoresist of Claim 11 further comprising a dissolution inhibitor.

22. A process for preparing a photoresist image on a substrate comprising, in order:

    (A)   applying a photoresist composition on a substrate to form a photoresist layer, wherein the photoresist composition comprises

30   (a) the copolymer of claims 1, 2, 3, 4, 5, 5a, 5b or 5c; and

       (b) at least one photoactive component;

    (B)   imagewise exposing the photoresist layer to form imaged and non-imaged areas; and

    (C)   developing the exposed photoresist layer having imaged and

35   non-imaged areas to form the photoresist image on the substrate.

23. The process of Claim 22 further comprising, between steps (A) and (B), a step of drying the photoresist composition to substantially remove solvent

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and thereby form the photoresist layer on the substrate, wherein the photoresist composition is further comprised of a solvent.

24. A use of a compound having a structure of $HCF_2CF_2OCH_2CH_2OCF_2CF_2H$ as a spin-coating solvent.
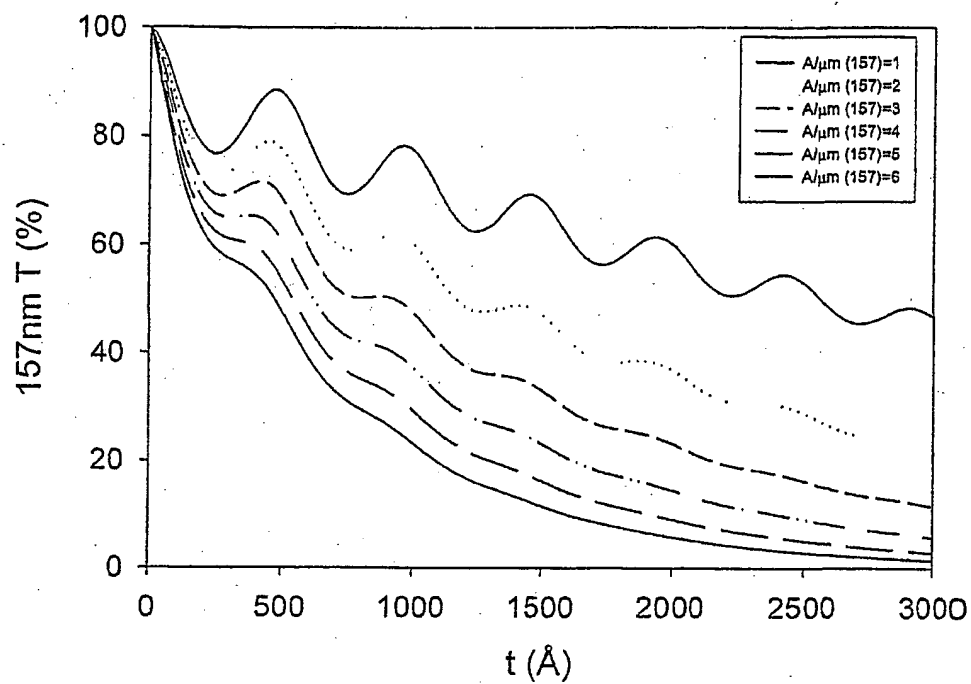
Figure 1
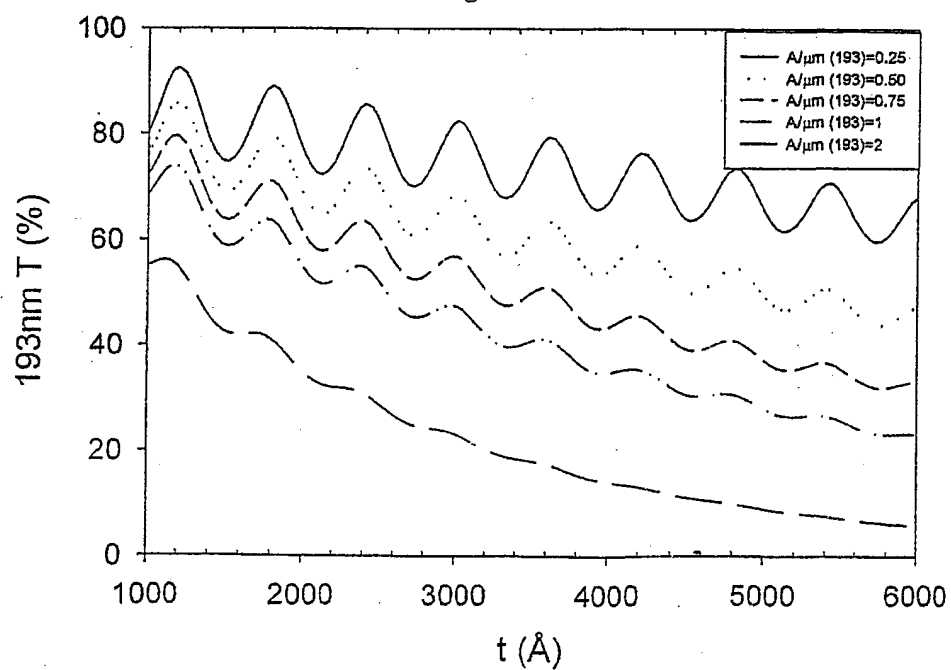
Figure 2
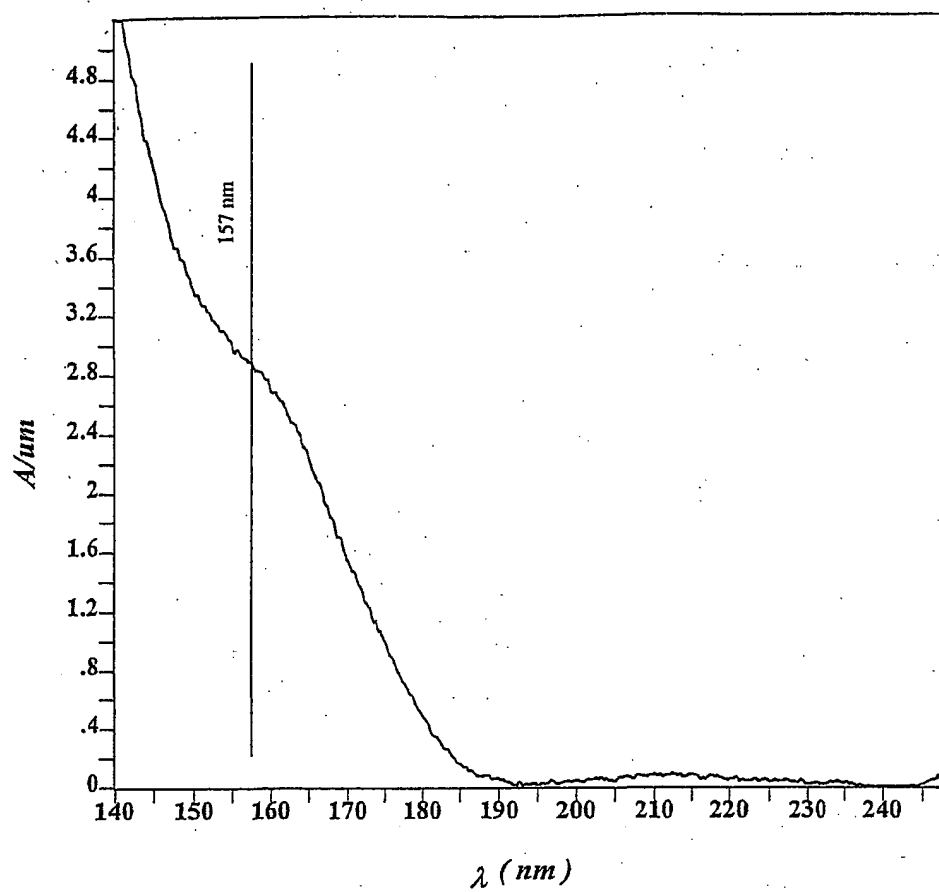
Figure 3

Example 1
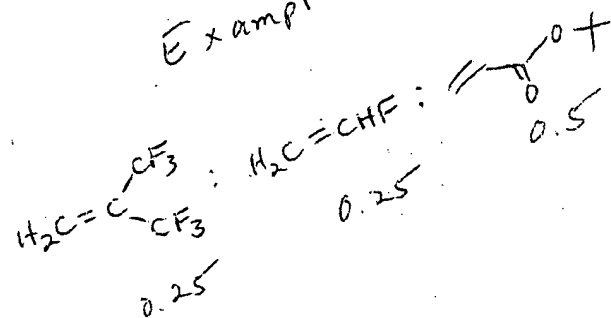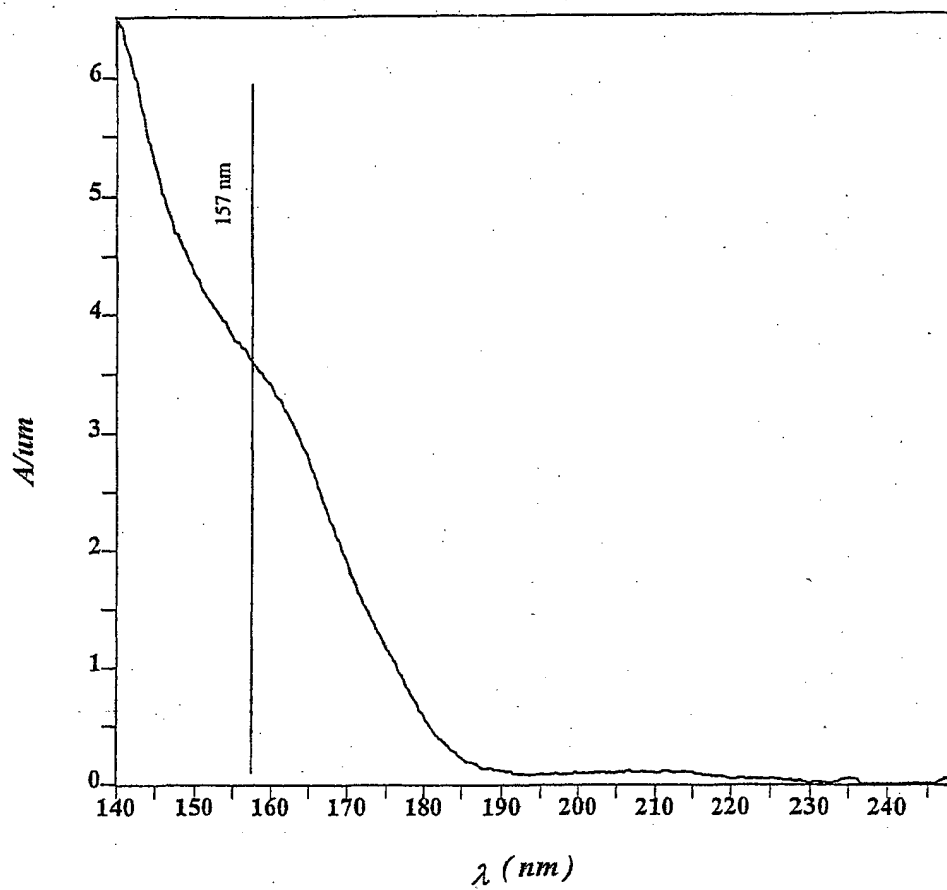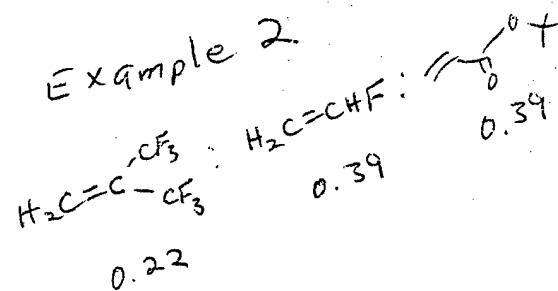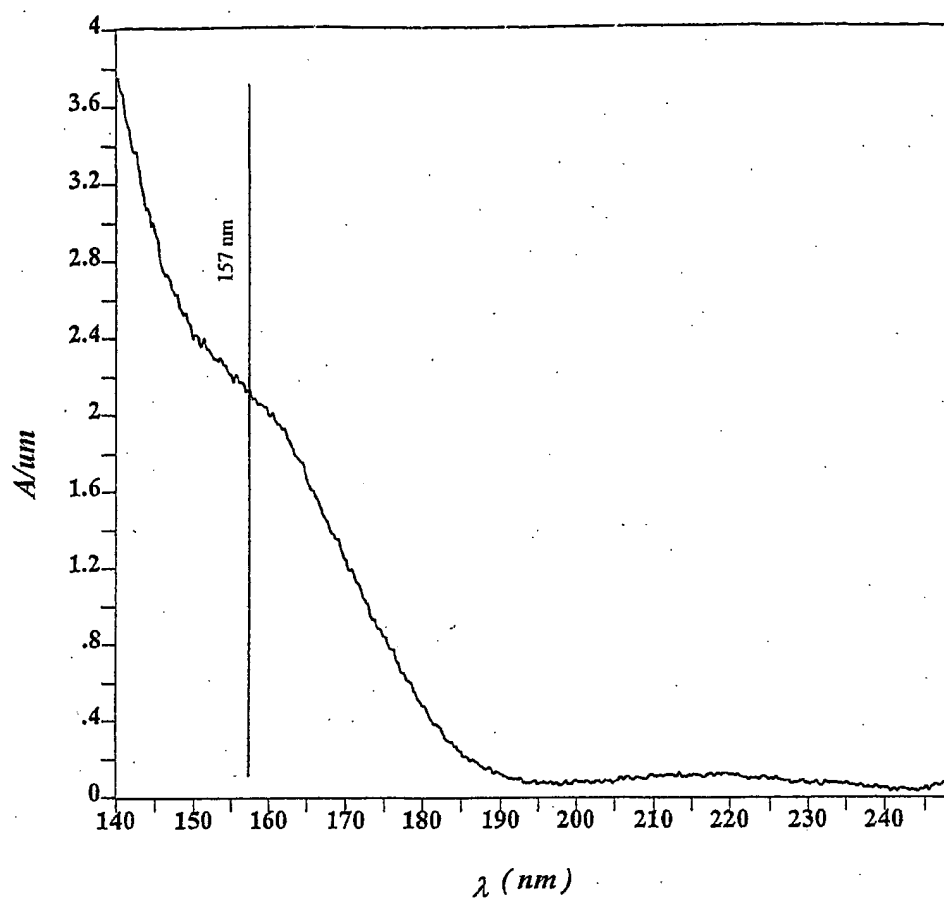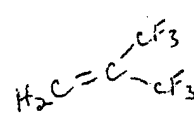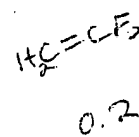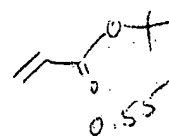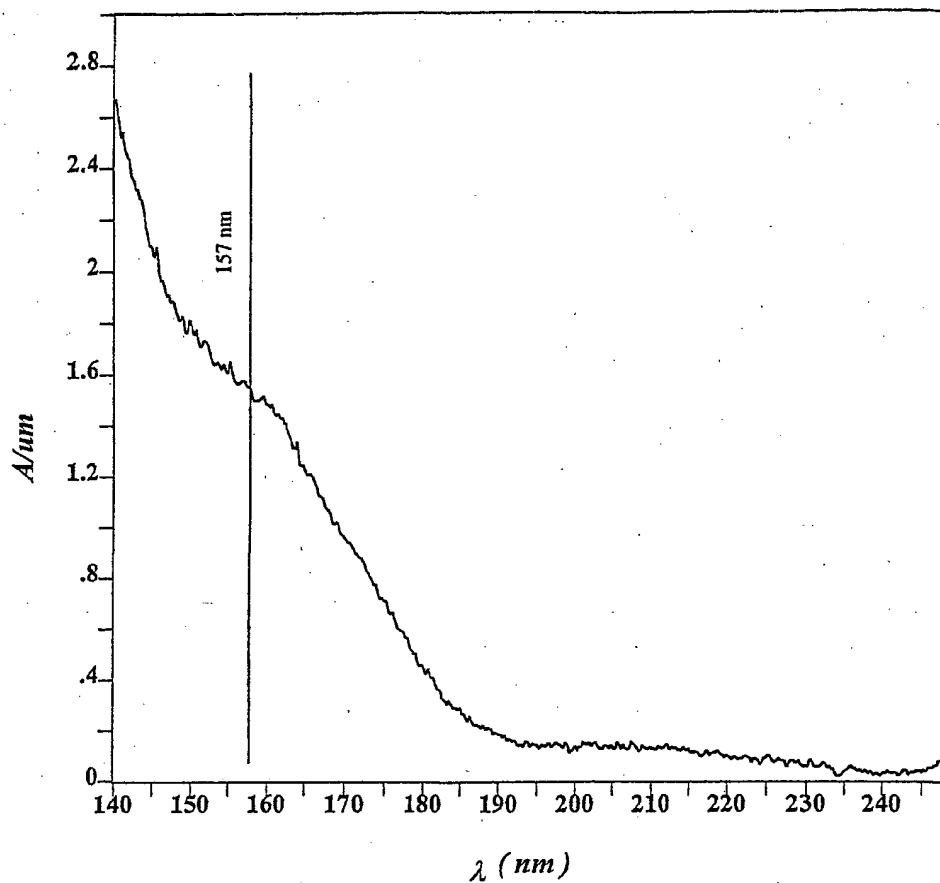
$H_2C=C\overset{-CF_3}{\underset{-CF_3}{\diagdown}}$: $H_2C=CHF$: $\diagup\overset{O}{\underset{O}{\diagdown}}O+$

0.25   0.25   0.5

$2.89 \ \mu m^{-1}$

Figure 4

Example 2.

$H_2C=C-CF_3$: $H_2C=CHF$:

0.22　　0.39　　0.39

3.64 μm^{-1}

Figure 5

Example 3

$H_2C = C \begin{matrix} -CF_3 \\ -CF_3 \end{matrix}$: $H_2C = CF_2$: (structure)

0.25   0.2   0.55

2.12 μm^{-1}

Figure 6

Example 4

$H_2C=C\begin{smallmatrix}CF_3\\CF_3\end{smallmatrix}$: $H_2C=CF_2$: 〜〜〜O

1.57 μm^{-1} 0.29   0.29   0.42

Figure 7

Figure 8

EX. 7

$H_2C = C - CF_3 \quad CF_3$

0.18

$4.33 \, \mu m^{-1}$

0.18

0.64

Figure 9

4.69 μm⁻¹

Example 8 (curve 8)

$H_2C=C-CF_3$ 0.27

CF_3

$F=F$ 0.27

CH_3 O

0.46
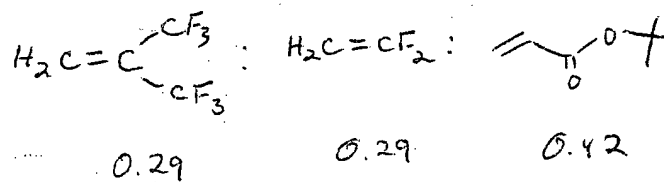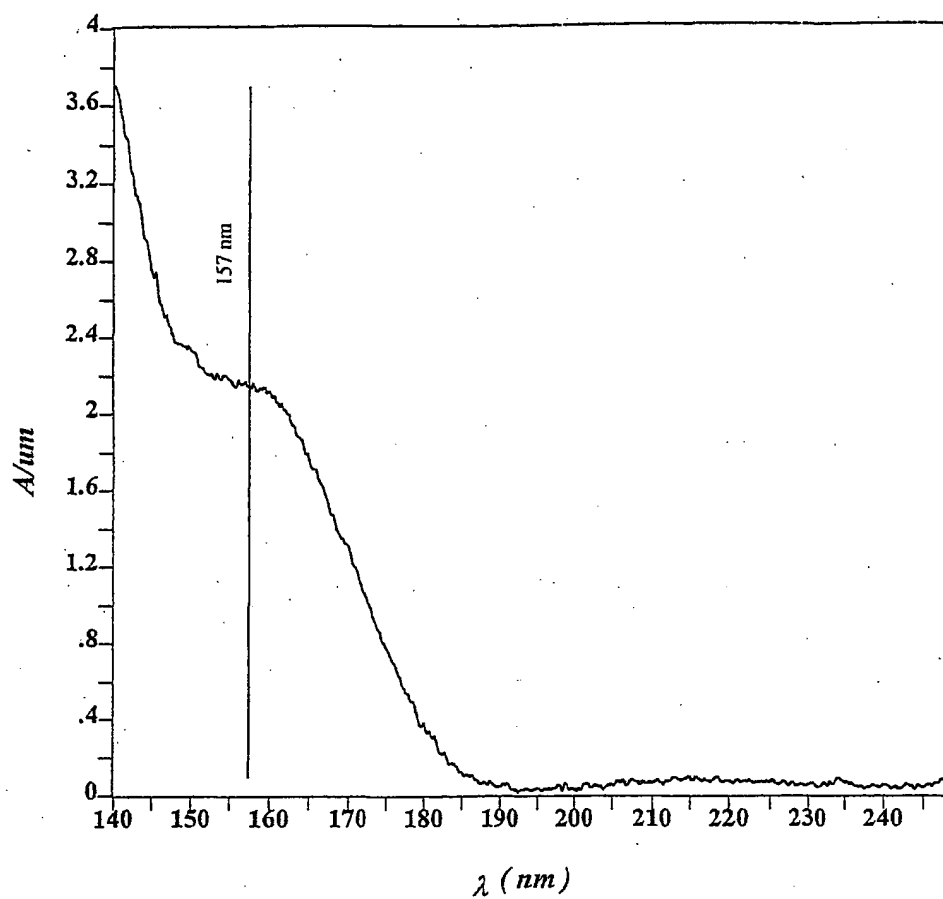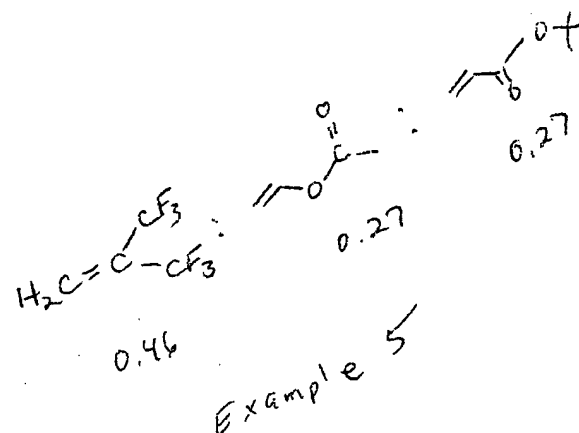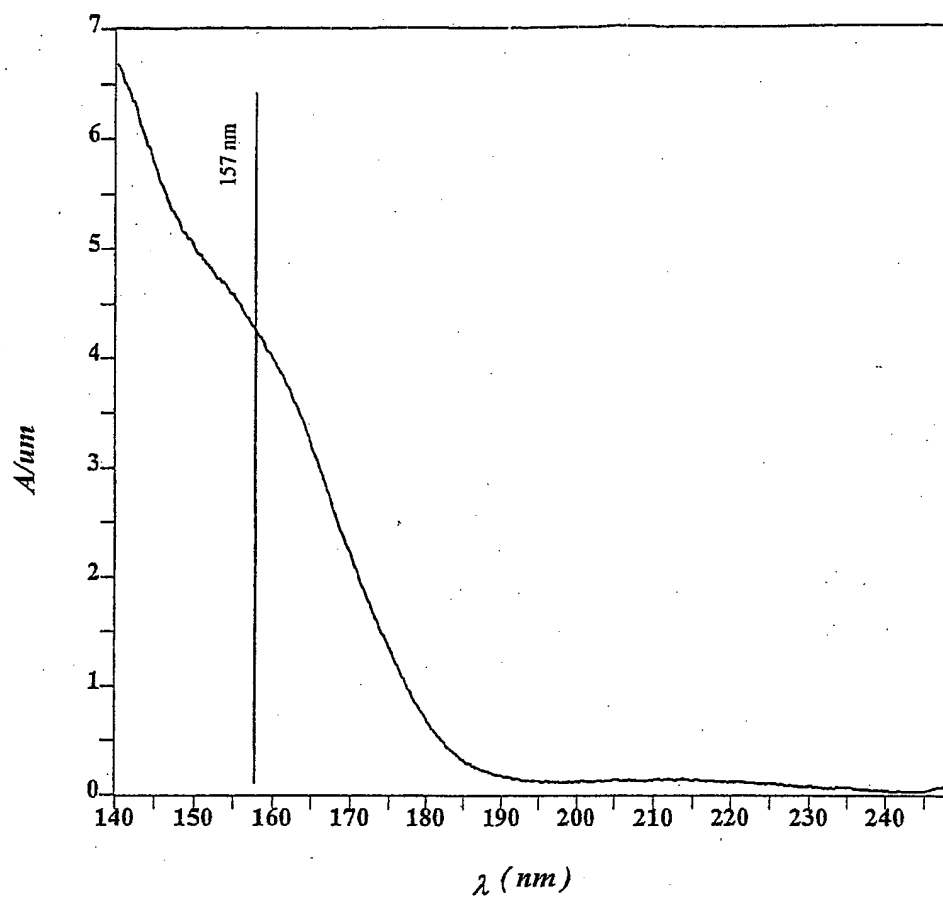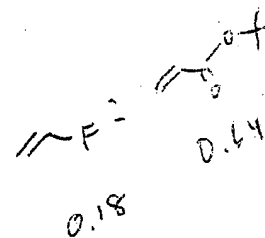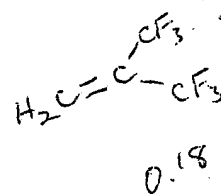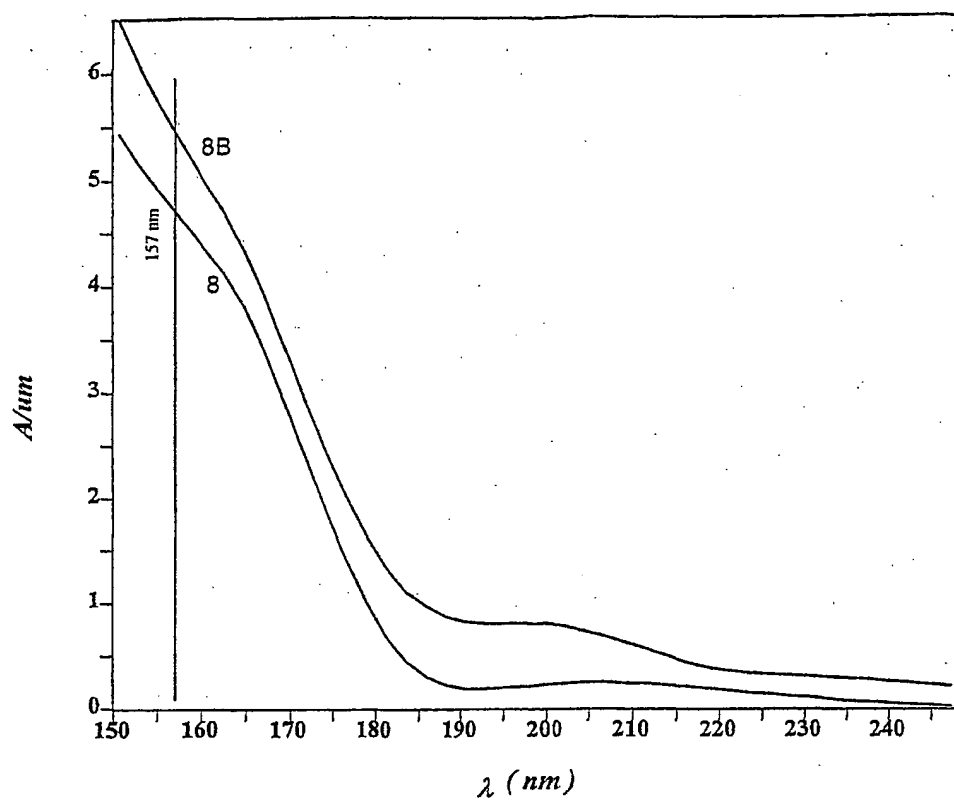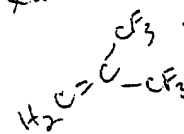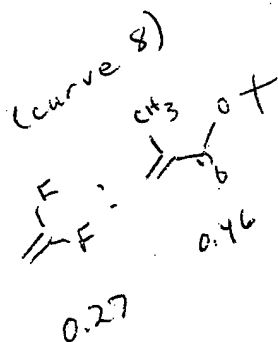
8B is
formulated
resist

Figure 10

4.40
5.37 μm⁻¹

Example 9

H₂C=C⁻CF₃ : F=F : CH₃O⁺
      ⁻CF₃   0.51
      0.23   0.26